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Title: Applications of Accelerated Molecular Dynamics in Materials Science

Author(s): Uberuaga, Blas P.

Intended for: Web

# Applications of Accelerated Molecular Dynamics in Materials Science

Blas Pedro Uberuaga

*Los Alamos National Laboratory*

Los Alamos NATIONAL LABORATORY EST.1943



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# Acknowledgements


- **Art Voter** (LANL)
- **Radiation damage in MgO:**
  - Kurt Sickafus (*now at Tennessee*)
  - Robin Grimes and Antony Cleave (*Imperial*)
  - Roger Smith and Pravesh Bacorisen (*Loughborough*)
  - Francesco Montalenti (*now at Milano*)
  - Graeme Henkelman (*now at UT Austin*)
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  - Xian-Ming Bai (*INL*)
  - Mike Nastasi (*now at Nebraska*)
  - Amit Misra and Richard Hoagland (*LANL*)
- **Radiation damage in pyrochlore:**
  - Kurt Sickafus (*now at Tennessee*)
  - Chao Jiang (*now at Wisconsin)*
  - Y Li (*Lanzhou University*)
  - Yong Wang and Samrat Choudhury (*LANL*)

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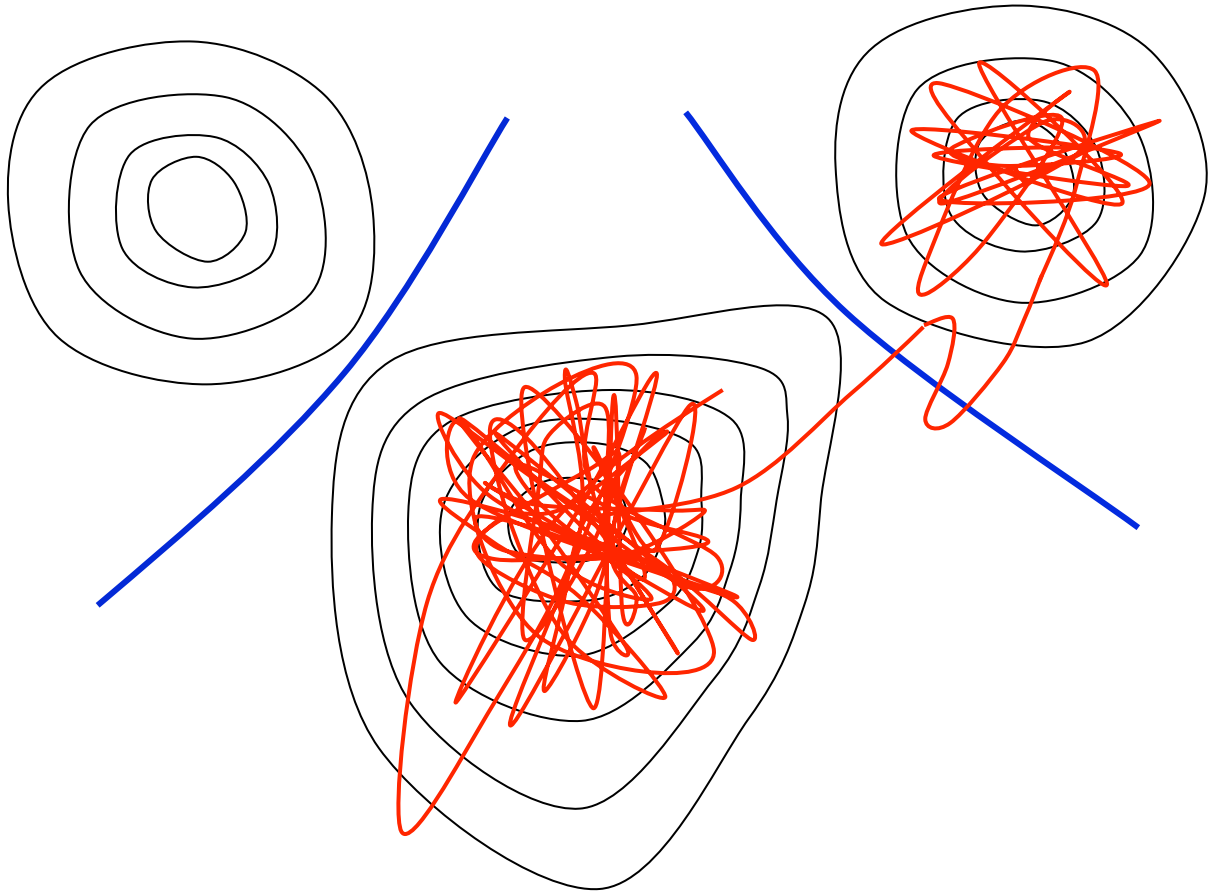
# INTRODUCTION TO AMD METHODS

# Brief Introduction to Accelerated Molecular Dynamics

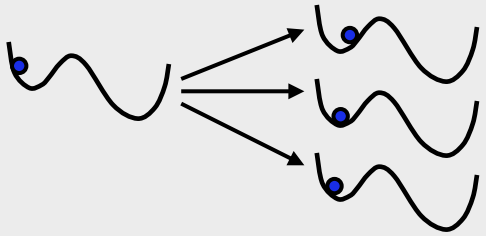
- Many processes occur on much longer timescales than accessible via MD (ps-ns-μs)
  - e.g. surface growth
  - radiation damage annealing
  - mass transport
  - etc.
- Need method to reach experimentally relevant timescales
- Three accelerated dynamics methods developed at LANL (Art Voter's team)
  - Parallel-Replica Dynamics
  - Hyperdynamics
  - Temperature Accelerated Dynamics (TAD)

# Infrequent Event System



- The system vibrates in 3N-dimensional basin
- Occasionally it escapes, crossing through a dividing surface to a new basin
- This behavior characterizes solid-state diffusion, as well as many other processes

# Accelerated Molecular Dynamics Methods

| | |
|---|---|
| **Parallel Replica Dynamics (1998)**  | Explore basin with many processors $M$ such that $M \sim \tau_{rxn}/1$ ps |
| | |
| | |

# Accelerated Molecular Dynamics Methods

| | |
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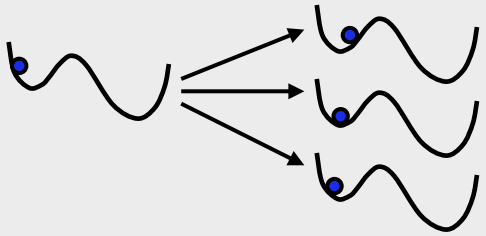
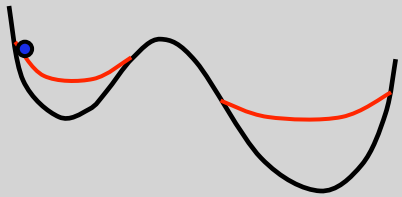
| **Parallel Replica Dynamics (1998)**  | Explore basin with many processors *M* such that $M \sim \tau_{rxn}/1$ ps |
| **Hyperdynamics (1997)**  | Increase rate by reducing effective barriers |
| | |

# Accelerated Molecular Dynamics Methods

| | |
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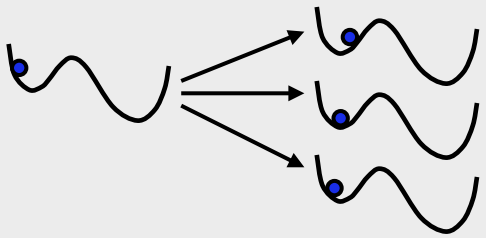
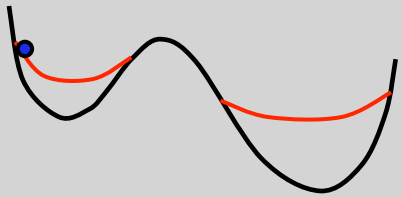
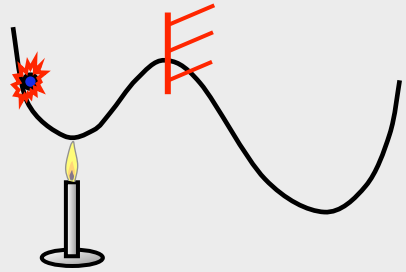
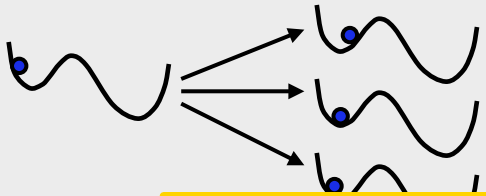
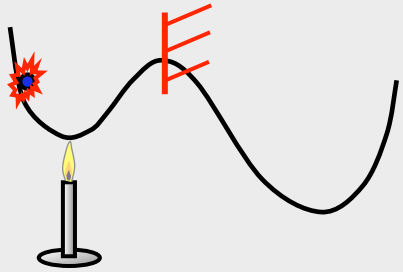
| **Parallel Replica Dynamics (1998)**  | Explore basin with many processors $M$ such that $M \sim \tau_{rxn}/1$ ps |
| **Hyperdynamics (1997)**  | Increase rate by reducing effective barriers |
| **Temperature Accelerated Dynamics (2000)**  | Increase rate by raising temperature |

# Accelerated Molecular Dynamics Methods

| | |
|---|---|
| **Parallel Replica Dynamics (1998)**  | Explore basin with many processors *M* such that $M \sim \tau_{rxn}/1$ ps |
| **Hyperdynamics**  | …cing |
| **Temperature Ac…**  | …ng temperature |

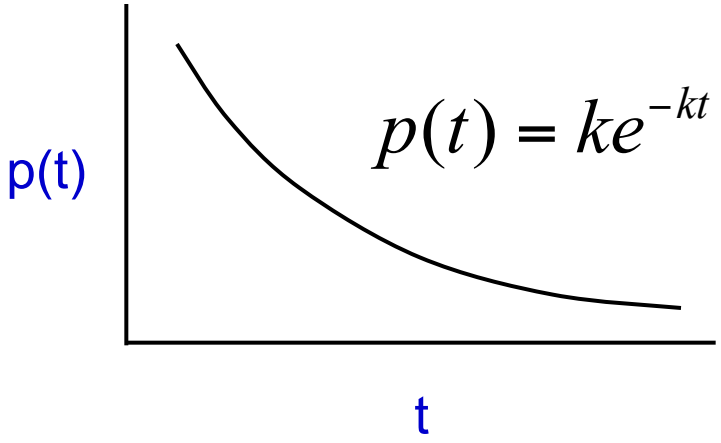
***Common Themes:***

- ***reduce waiting time for a transition to order of picoseconds***
- ***let the trajectory find an appropriate way out of state, but coax it into doing so more quickly***

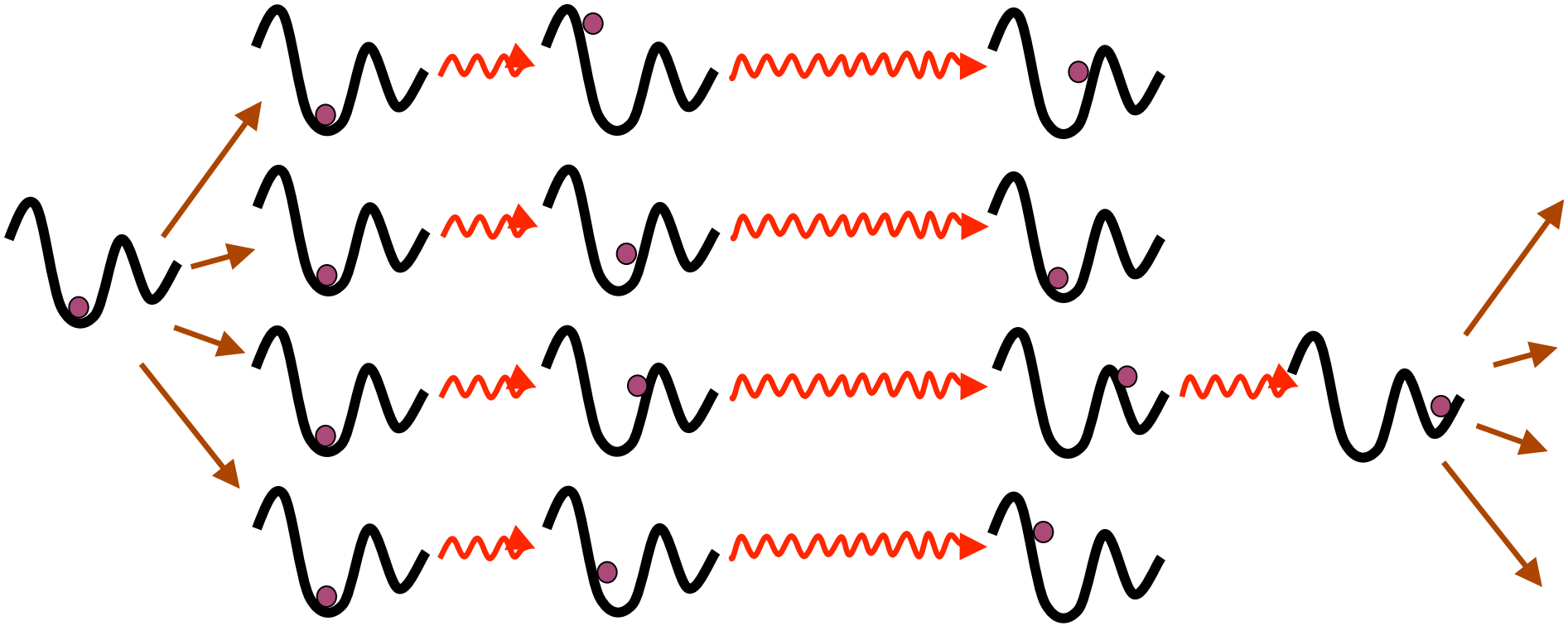
# Introduction to Parallel-Replica Dynamics

Voter, *PRB* **57**, R13985 (1998)

- Offers parallel speed-up in simulation time
  - Not as “glamorous” as other methods which offer exponential speed-up on a single processor
- However, parallel-replica can be applied to systems not suited to the other methods
  - Rough potentials
  - Floppy systems with fast transitions
  - Driven systems
- Assumptions:
  - infrequent events
  - transitions can be detected
  - correlation time known
  - distribution of first-escape times is exponential

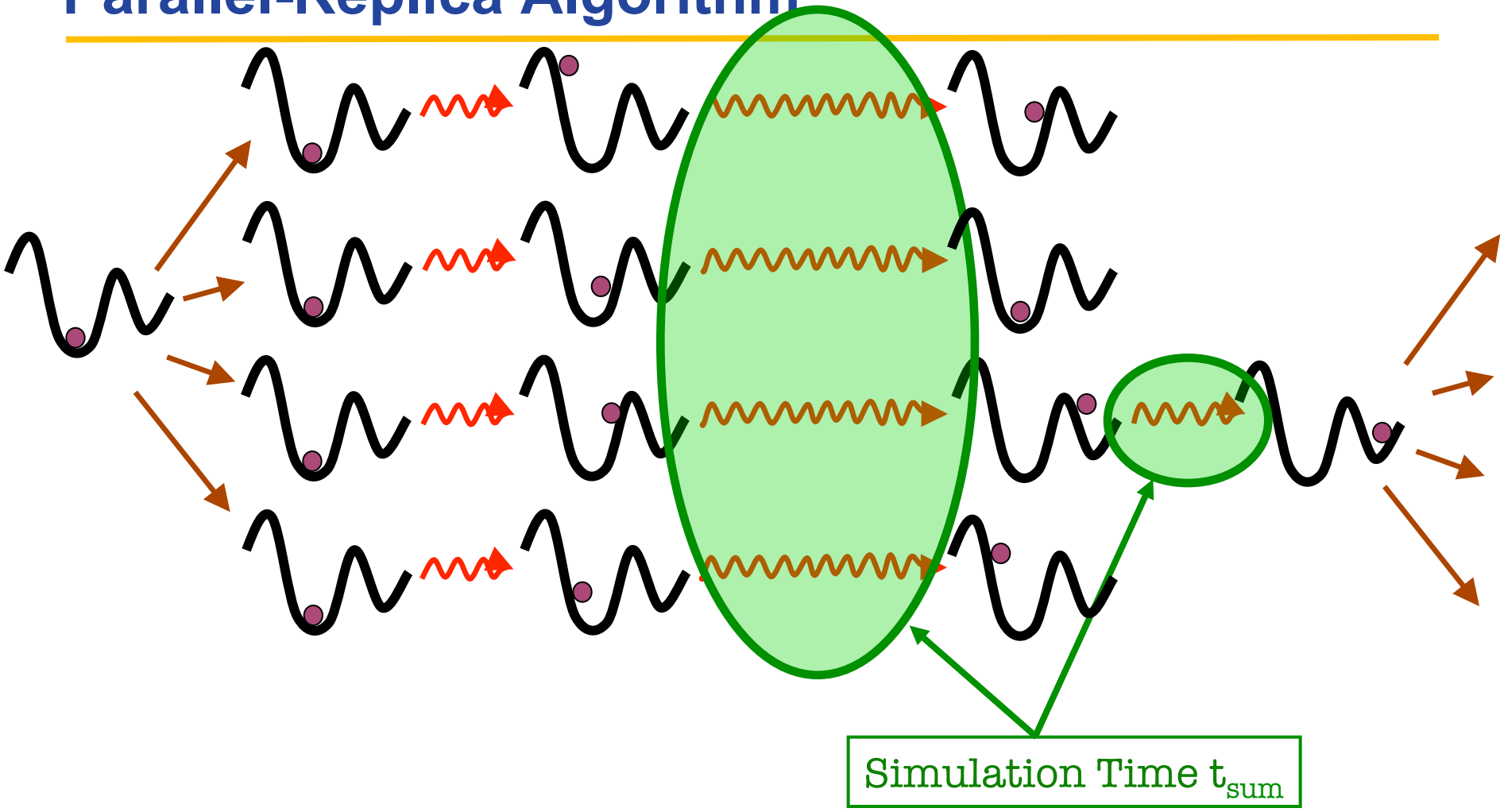


# Parallel-Replica Algorithm

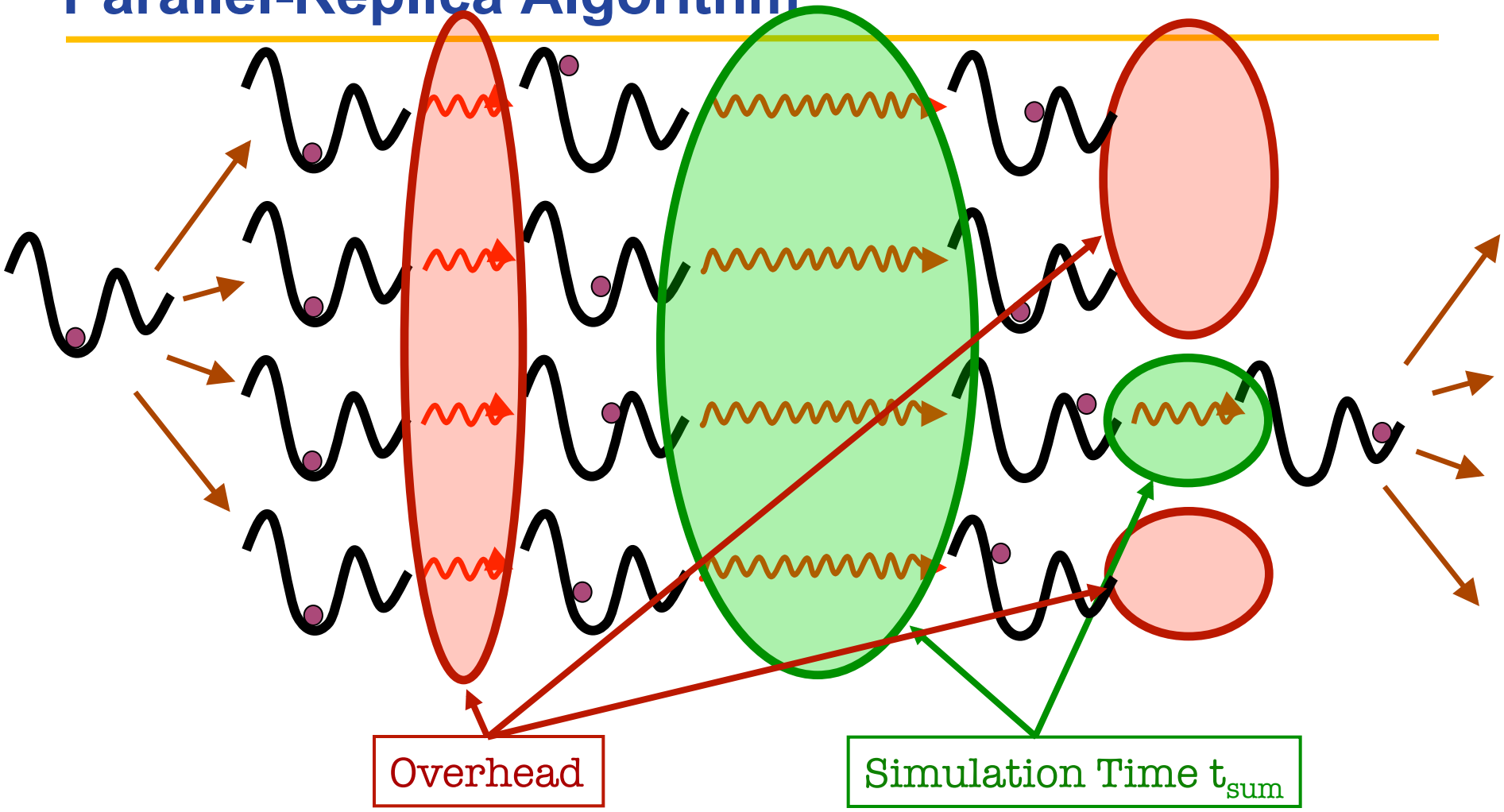


➔ Exact Longtime Dynamics

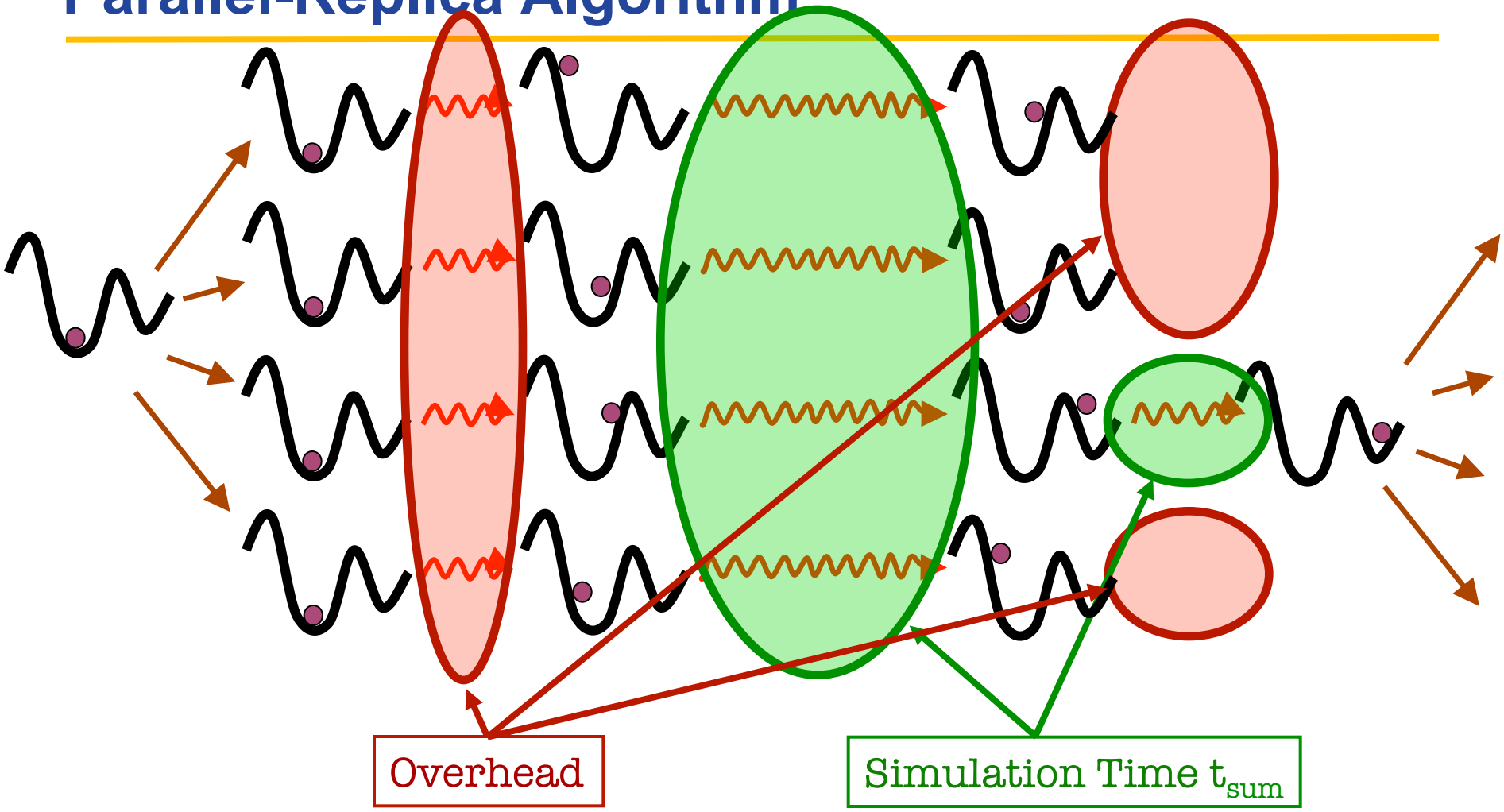
# Parallel-Replica Algorithm



# Parallel-Replica Algorithm



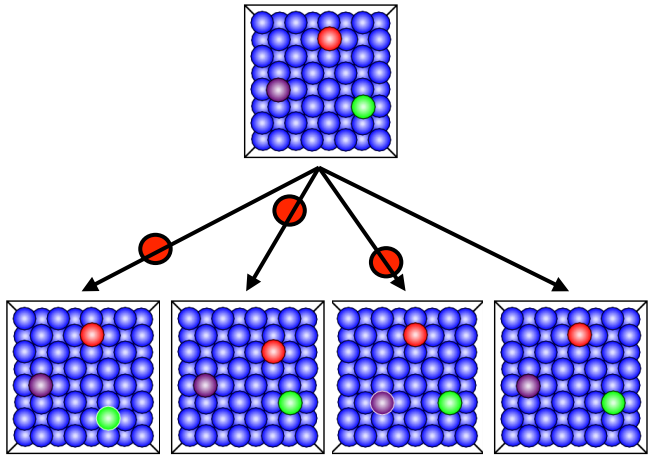
# Parallel-Replica Algorithm




**Good parallel efficiency if $t_{rxn} / M >> \tau_{dephase} + \tau_{corr}$**

# Comparison of Parallel Algorithms

Standard MD

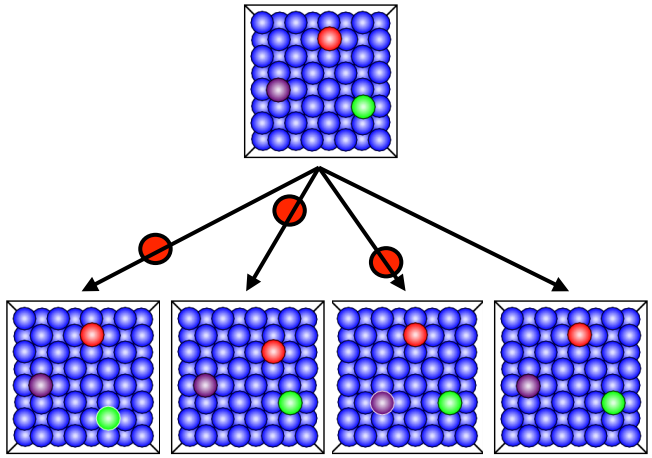


M simulations of
size N for time t

● = event

# Comparison of Parallel Algorithms

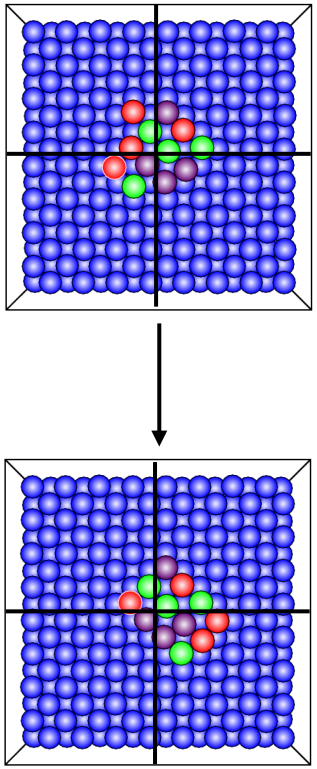
Standard MD



M simulations of size N for time t

● = event

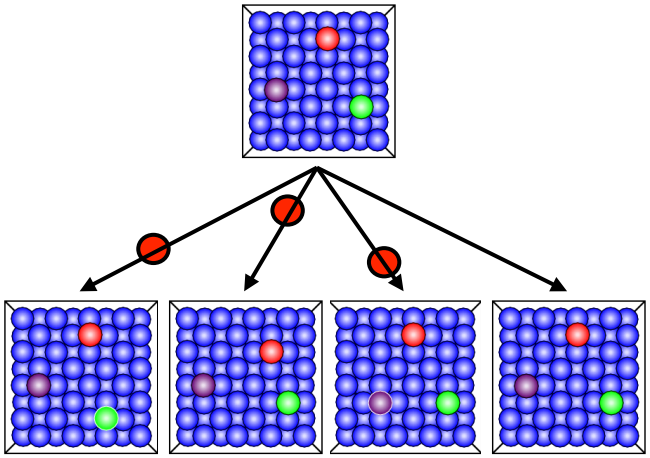
Spatial Parallelization



1 simulation of size MN for time t

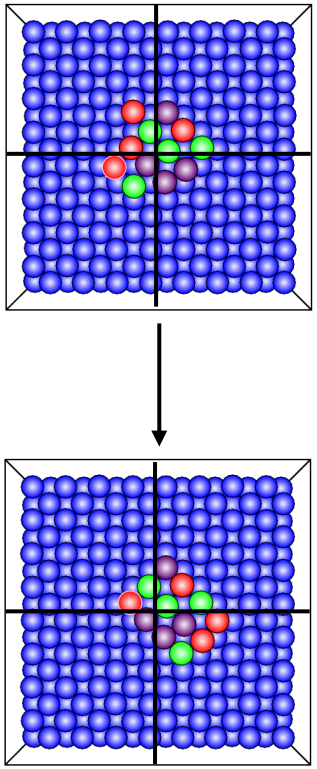
# Comparison of Parallel Algorithms

Standard MD



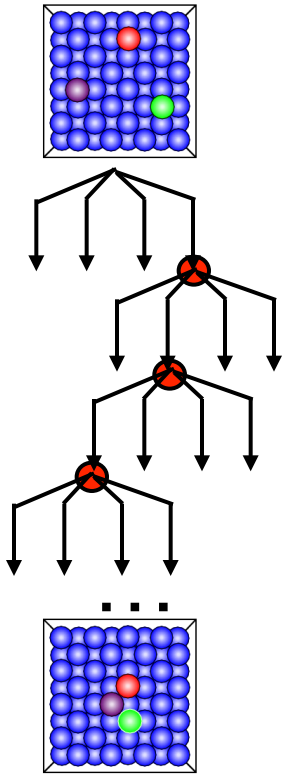
M simulations of size N for time t

Spatial Parallelization



1 simulation of size MN for time t

Parallel-Replica

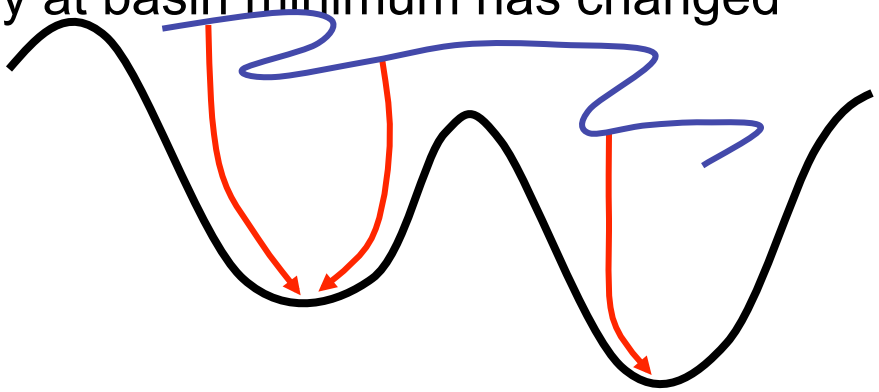


1 simulation of size N for time Mt

= event

# Detecting a Transition

- Best method depends on the system
- Simple method for EAM metal systems:
  - periodically perform minimization
  - see if geometry at basin minimum has changed



- Other Methods:
  - change in bond connectivity/length (covalent systems) (Kum, Uberuaga)
  - change in energy fluctuations (Pande)

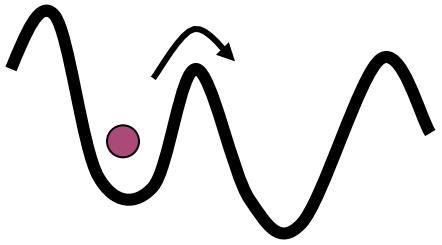
# Summary - Parallel-Replica Dynamics

- Most exact of the accelerated dynamics methods
  - no harmonic approximation
  - goes beyond TST to include correlated dynamical events
  - no assumption that barrier is energetic - can be entropic
- Easy to implement – requirements:
  - transition detection
  - good estimate of correlation time
- Very general applicability
  - any system with exponentially distributed events
- Good match to increasing availability of parallel processing power, distributed computing, etc.

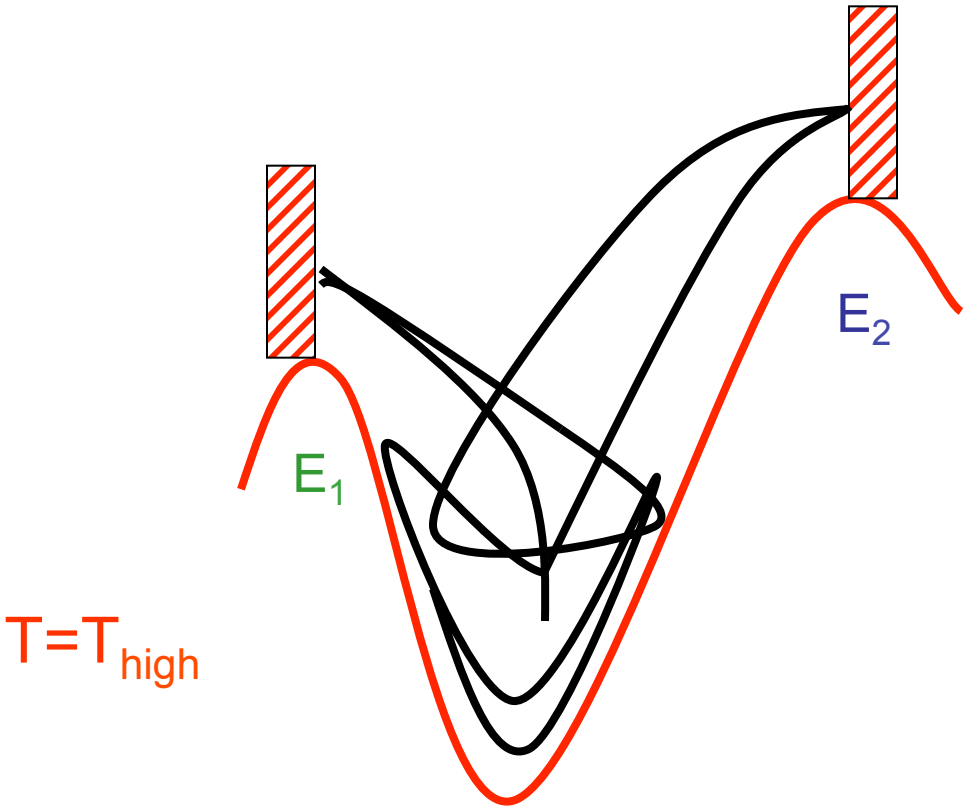
Sørensen and Voter,
*JCP* **112**, 9599 (2000)

# Introduction to Temperature Accelerated Dynamics (TAD)

- Concept:
  - System characterized by deep energy wells
  - Run basin constrained MD at high temperature
  - Extrapolate behavior to low temperature
- Approximations: $\left( k = \nu e^{-\Delta E / k_B T} \right)$
  - Harmonic Transition State Theory
  - Assumed minimum prefactor in system $\nu_{min}$
  - Uncertainty level $\delta$ of missing the correct event
- Very powerful when barriers are high relative to temperature

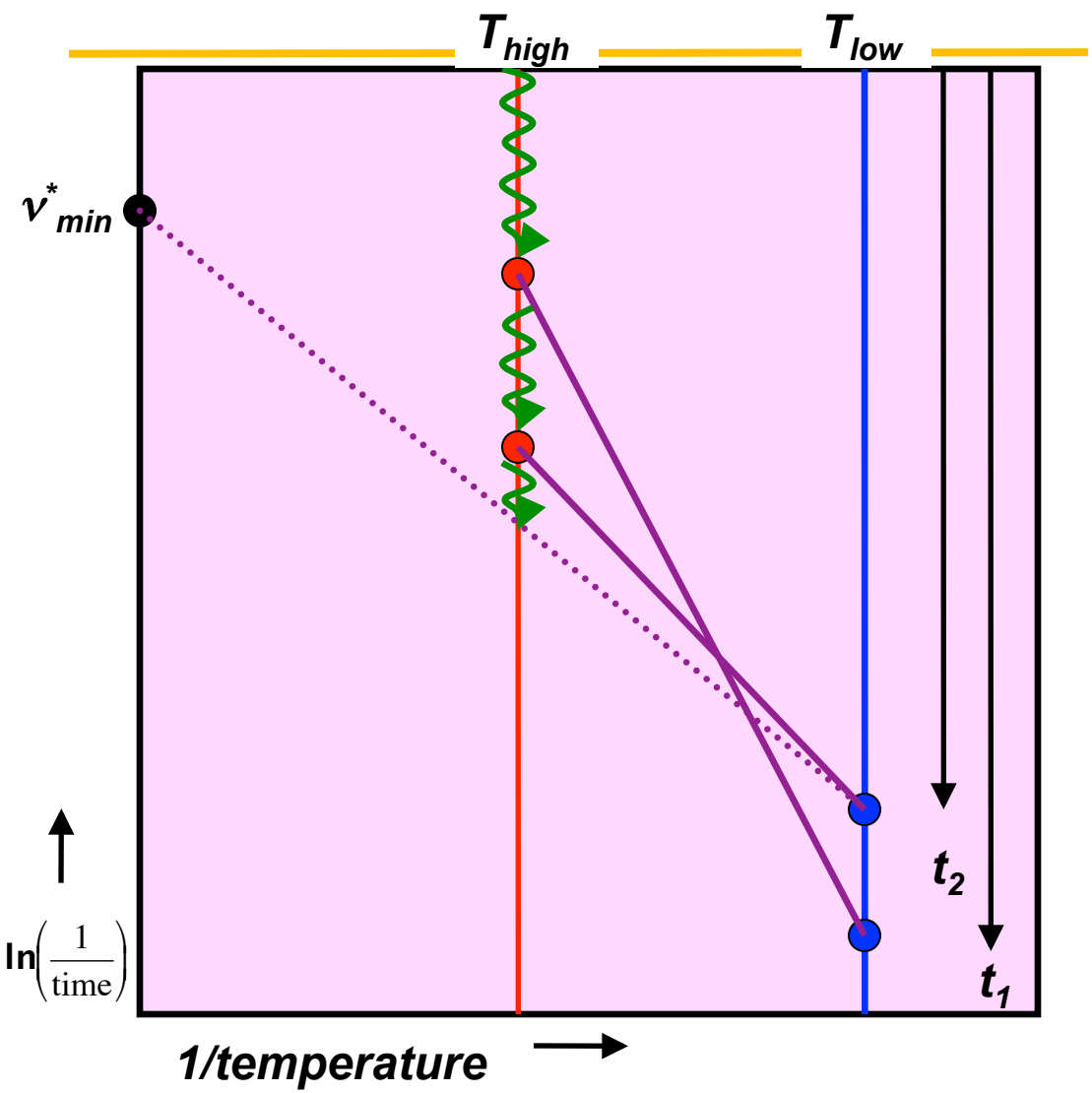


# Basin Constrained MD (BCMD)




- Run dynamics at $T_{high}$
- When event occurs, reflect trajectory back into basin
- Continue high-T dynamics
- Reflect trajectory after any other events
- Requires:
  - Detecting transition
  - Finding energy barrier

# TAD algorithm




- Do MD at $T_{high}$ until see an event
- Find barrier, extrapolate to $T_{low}$, find time $t_1$
- Continue at $T_{high}$ to next event
- Find barrier, extrapolate to $T_{low}$, find time $t_2$
- Continue at $T_{high}$ until earlier event not possible (within $\delta$)
- Accept event with earliest time ($t_2$)

# Summary - Temperature Accelerated Dynamics

- Potentially most powerful AMD method
  - Extremely large boosts when temperature is small compared to barriers

- Basic algorithm is easy to implement – requirements:
  - transition detection
  - Basin constrained MD
  - Saddle finding method

- Defect Dynamics in MgO
- Vacancy Void Annealing in Cu
- Damage production and evolution near grain boundaries
- Defect production and recovery in pyrochlore

# DEMONSTRATIONS OF AMD METHODS

**Common Theme:**
***Examples where achieving long times in atomistic simulations provided critical insight into defect mechanisms important for understanding radiation damage***

- Defect Dynamics in MgO
- Vacancy Void Annealing in Cu
- Damage production and evolution near grain boundaries
- Defect production and recovery in pyrochlore

# DEMONSTRATIONS OF AMD METHODS

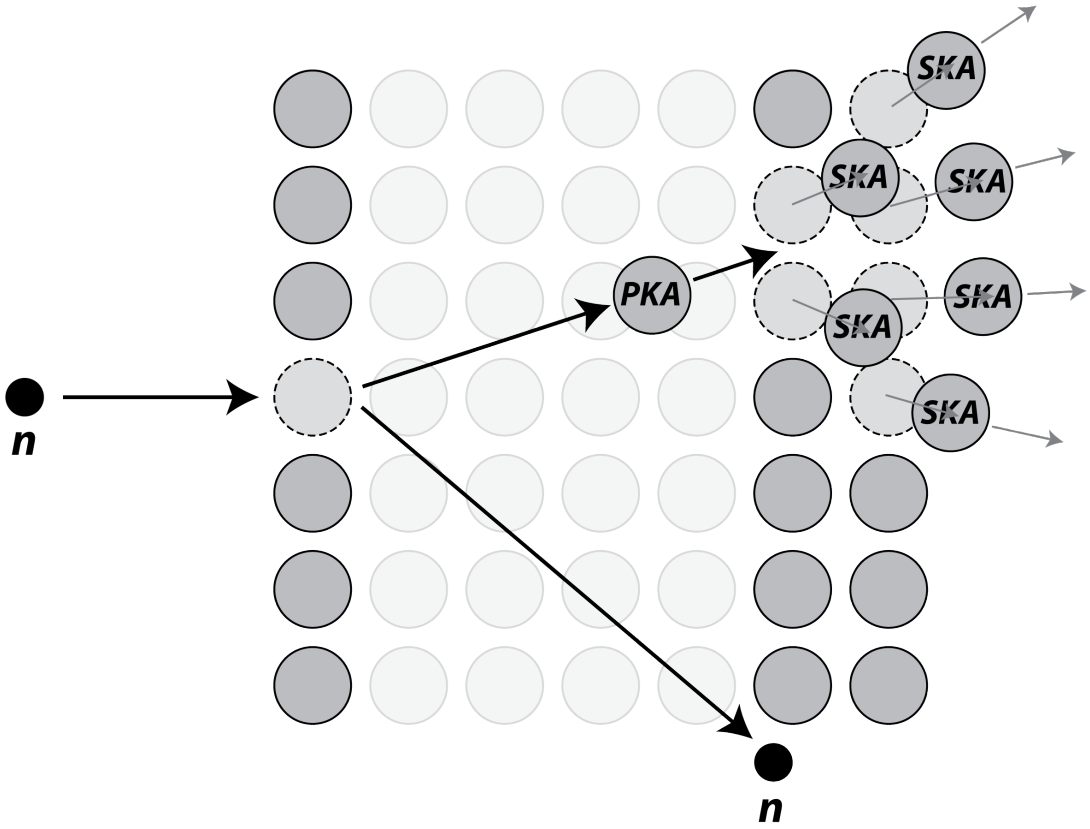
# INTRODUCTION TO RADIATION DAMAGE

# Radiation Damage Concepts

- Displacive radiation damage results in formation of *Frenkel (interstitial-vacancy) pair* defects in the lattice.
- The concentration of defects in an irradiated material far exceeds the equilibrium thermodynamic concentration of defects.
- The radiation damage response of a material is determined by the fate of these excess defects in the lattice.

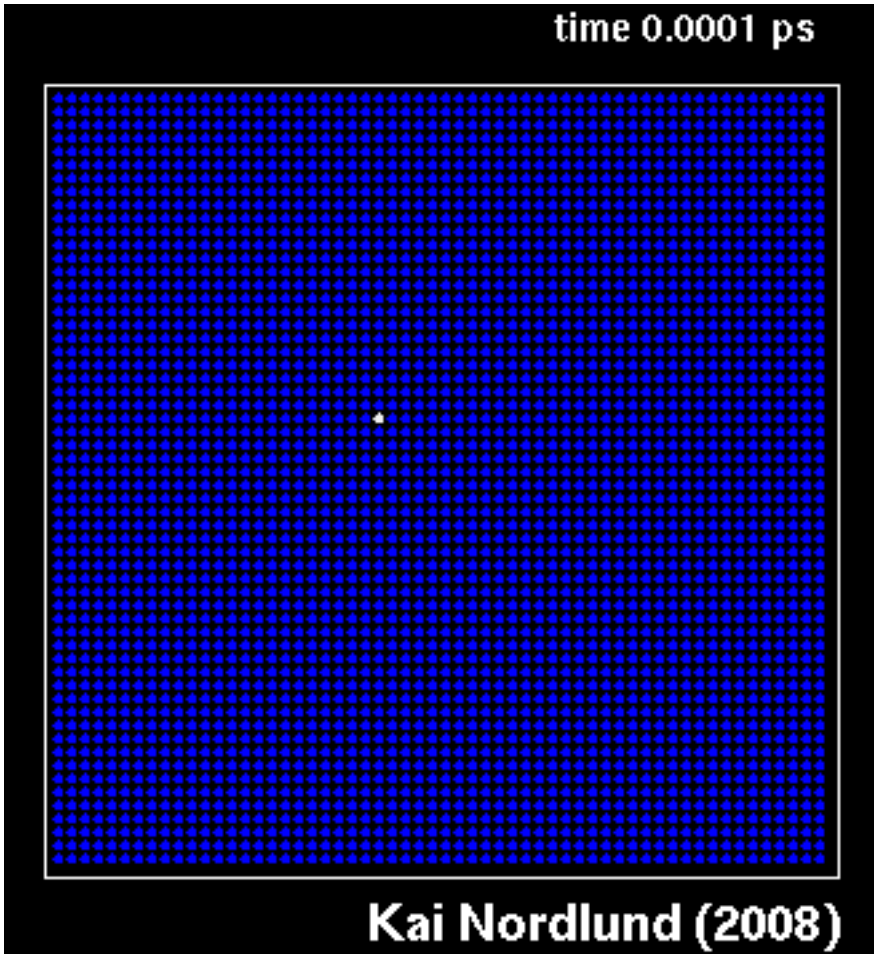
# Radiation damage event

- Kinetic energy deposited in a crystal by a fast neutron (*n*)
- The neutron imparts kinetic energy to an atom, displacing it. This atom is the primary knock-on atom (*PKA*)
- The *PKA* displaces additional atoms, secondary knock-on atoms (*SKAs*)
- The collection of displaced atoms is referred to as a displacement cascade



# Displacement, or Collision, Cascade

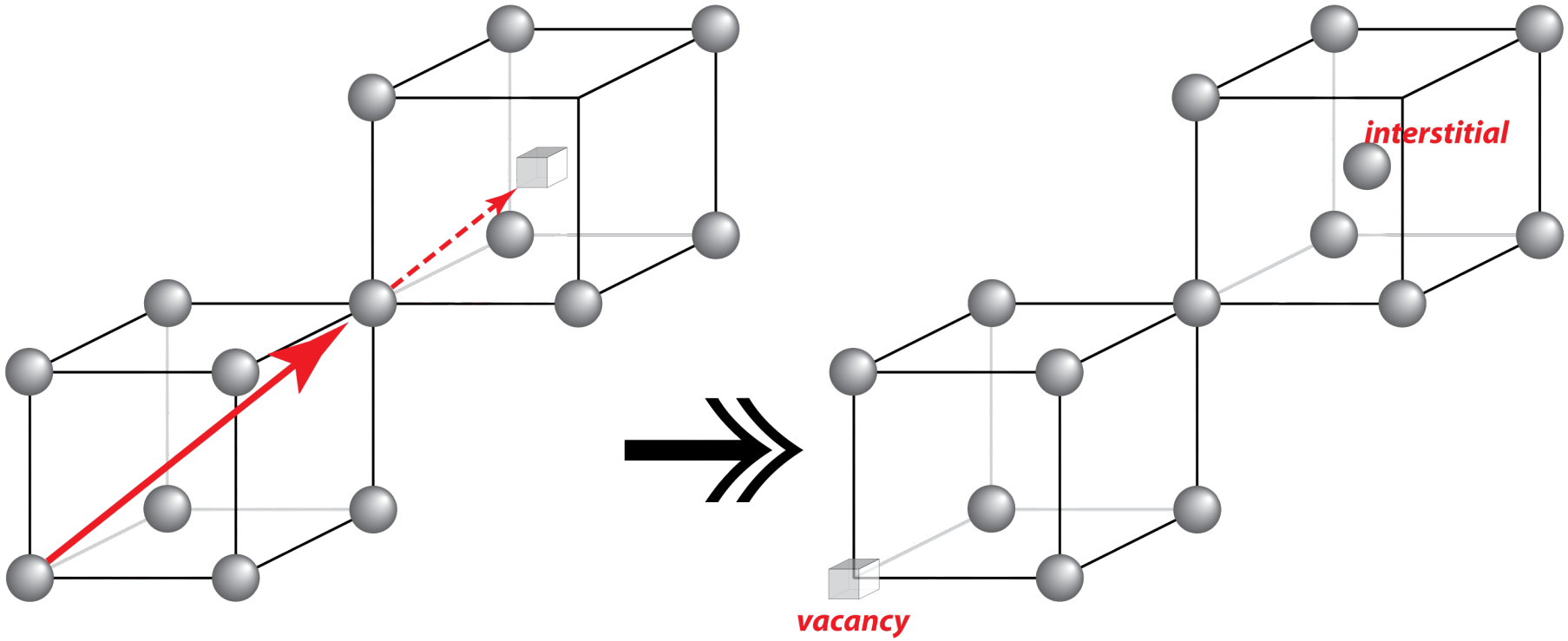
- The displacement of many atoms in the lattice results in a collision cascade
- Most atoms find lattice sites, but a few remain displaced, creating defects in the lattice
  - Defects are primarily interstitials and vacancies



# *Frenkel Pair* (i-v pair) Formation Under Irradiation

**Before displacement**

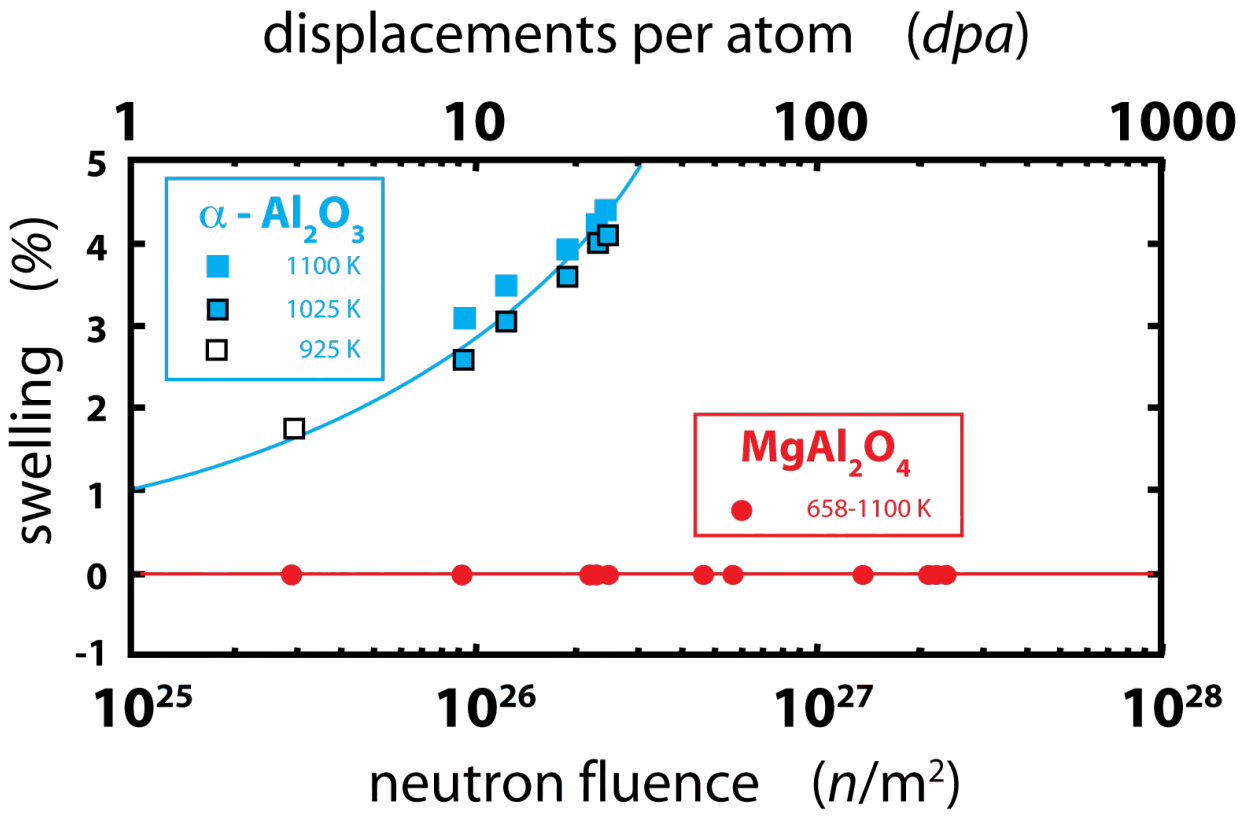
**After displacement**



# Radiation Damage Evolution

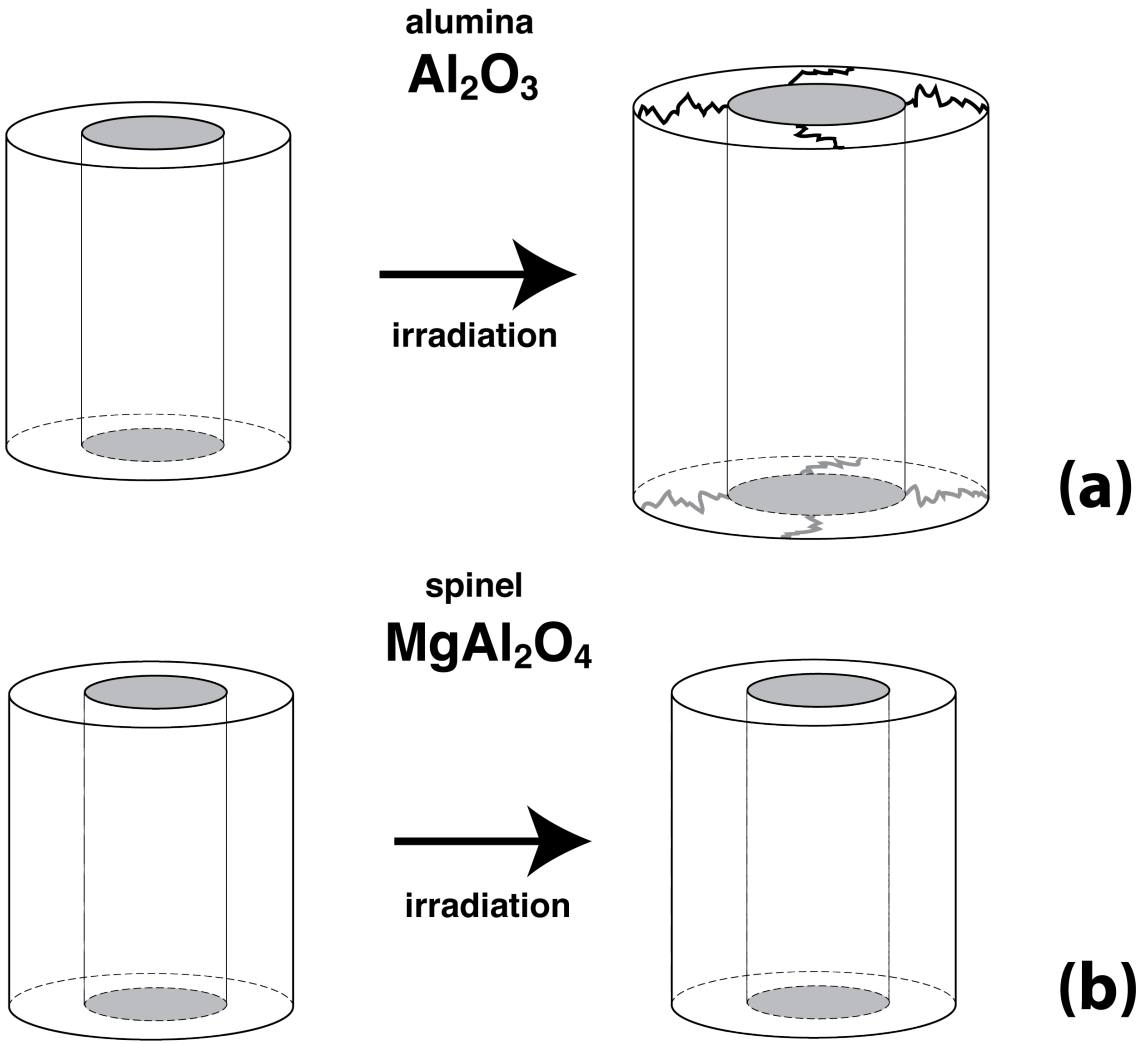
- Radiation damage is a competition between
  - The harmless annihilation of irradiation-induced point defects by i-v recombination
  - The harmful condensation of point defects to form extended lattice defects such as dislocation loops and voids.
- These damage mechanisms are at crossed purposes:
  - The first restores the perfect crystal lattice
  - The second disrupts the lattice by introducing detrimental large-scale imperfections.
- Much of the field of radiation damage research is devoted to developing an understanding of the interplay between these radiation damage mechanisms.

# Volumetric swelling versus fast neutron fluence for two engineering oxide ceramics: α-$Al_2O_3$ and $MgAl_2O_4$




C. Kinoshita and S. J. Zinkle, "Potential and limitations of ceramics in terms of structural and electrical integrity in fusion environments," J. Nucl. Mater. **233-237** (1996) 100-110.

# Consequences of Swelling: Schematic



# Consequences of Swelling: Real Materials

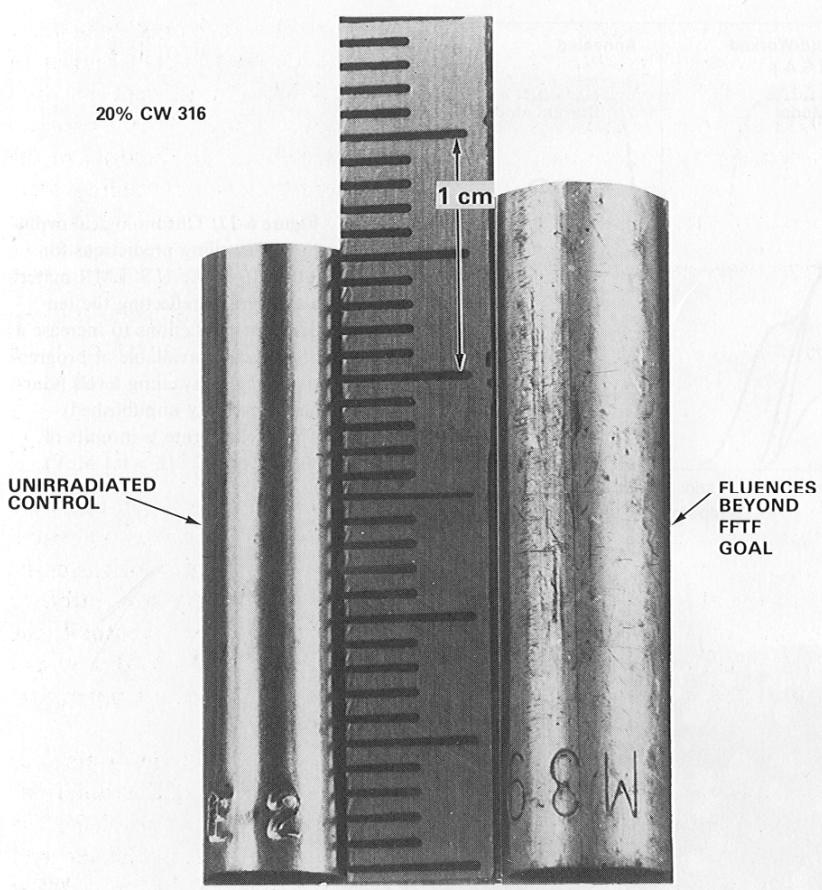



**Figure 6-24.** Easily observed swelling (≈10% linear, ≈33% volumetric) in unfueled 20% cold worked AISI 316 cladding tube at $1.5 \times 10^{23}$ n cm$^{-2}$ ($E > 0.1$ MeV) or ≈75 dpa at 510°C in EBR-II (after Straalsund et al., 1982). Note that, in the absence of physical restraints, all relative proportions are preserved during swelling.

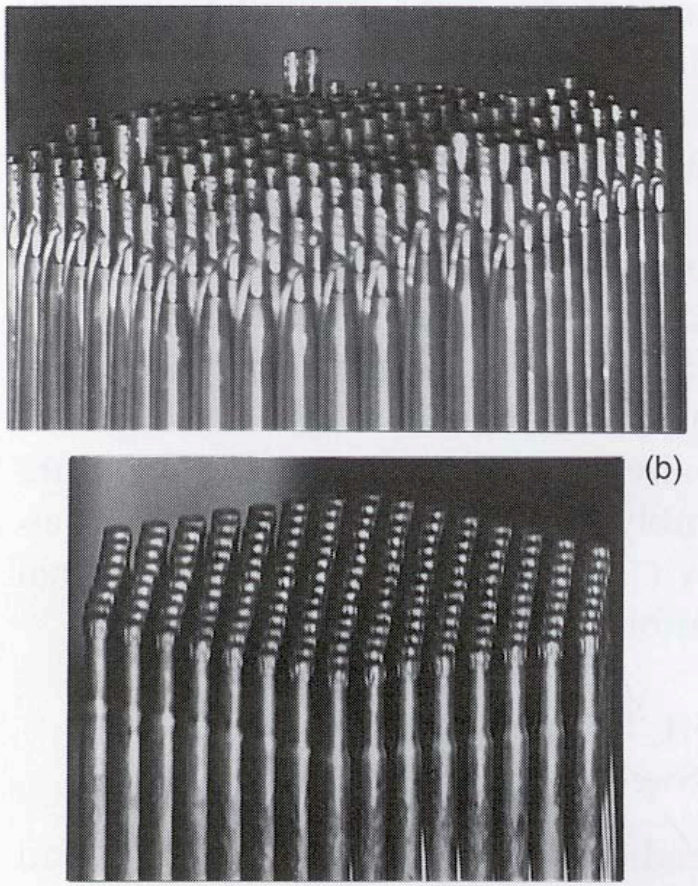



**Figure 6-131.** (a) Top of a bundle of D9 fuel pins irradiated to a peak fluence of $2.1 \times 10^{23}$ n cm$^{-2}$ ($E > 0.1$ MeV), showing varying length of pins in response to gradients across the bundle in flux and temperature and also to small variations in pin fabrication history and composition. (b) An undistorted fuel pin assembly with nonswelling HT9 cladding at $1.9 \times 10^{23}$ n cm$^{-2}$ ($E > 0.1$ MeV) (after Makenas et al., 1990 a).

Ref: Garner, Ch. 6, Irradiation Performance of Cladding and Structural Steels in Liquid Metal Reactors, of “Nuclear materials part 1”, Vol10A, Published by VCH, Germany

# Keys to understanding radiation damage

- Evolution of material under irradiation directly tied to fate of defects
- Whether defects annihilate or aggregate determines if material survives or fails
- Key factors include:
  - Defect mobility
  - Defect clustering
  - Defect interactions with microstructure (interfaces, dislocations)
- Atomistic simulations can provide critical insight

A Temperature Accelerated Dynamics Study

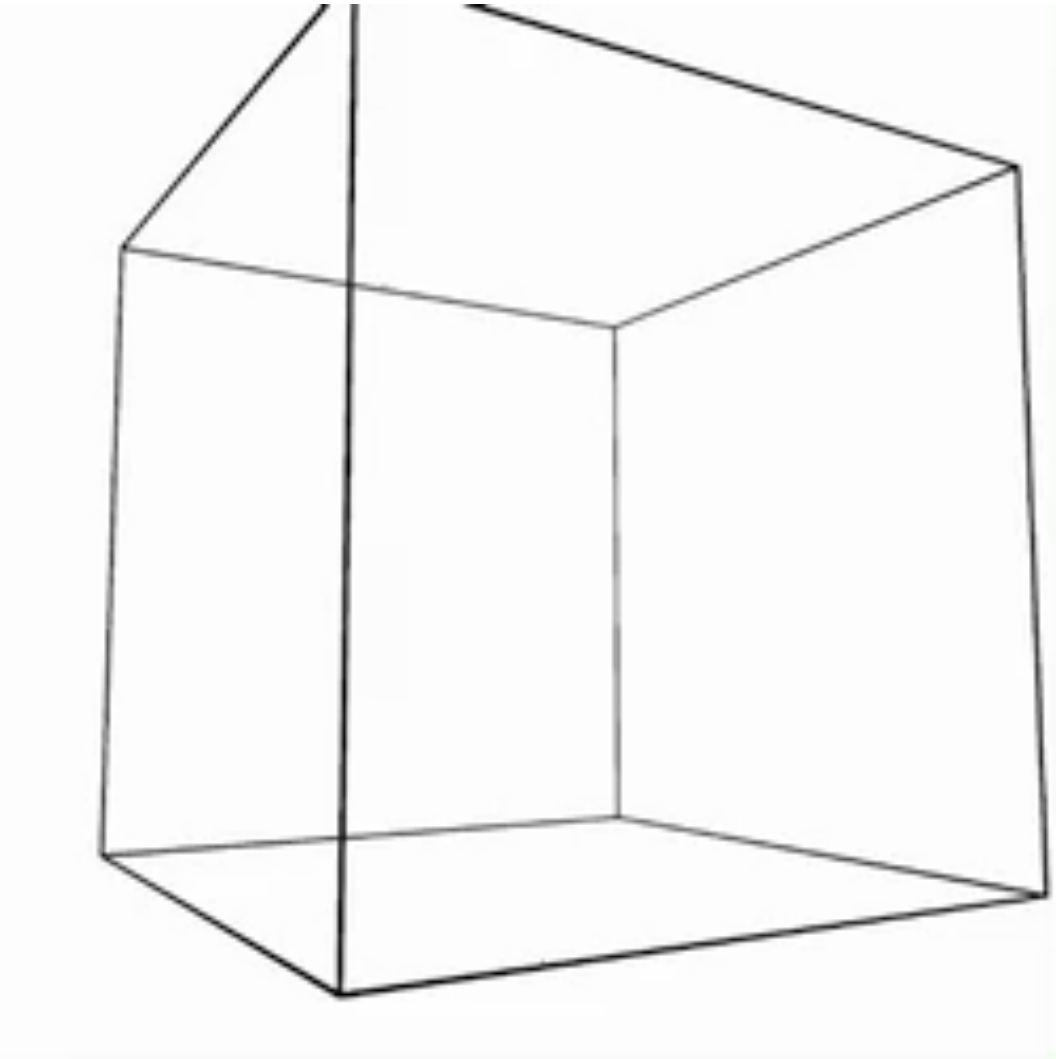
# DEFECT DYNAMICS IN MgO

# Defect Dynamics in MgO

- Goal:
  - Understand origin of radiation tolerance in complex oxides
  - Determine the relevance of metastable defects
- Methods:
  - Buckingham potential with long range electrostatics
  - MD: non-equilibrium production of damage due to irradiation
  - TAD: evolution of defects produced under irradiation
  - Rate theory: impact of atomistic defect properties on experimental observables
- References:
  - Uberuaga, Smith, Cleave, Henkelman, Grimes, Voter, and Sickafus, PRL **92**, 115505 (2004); PRB **71**, 104102 (2005); NIMB **28**, 260 (2005).

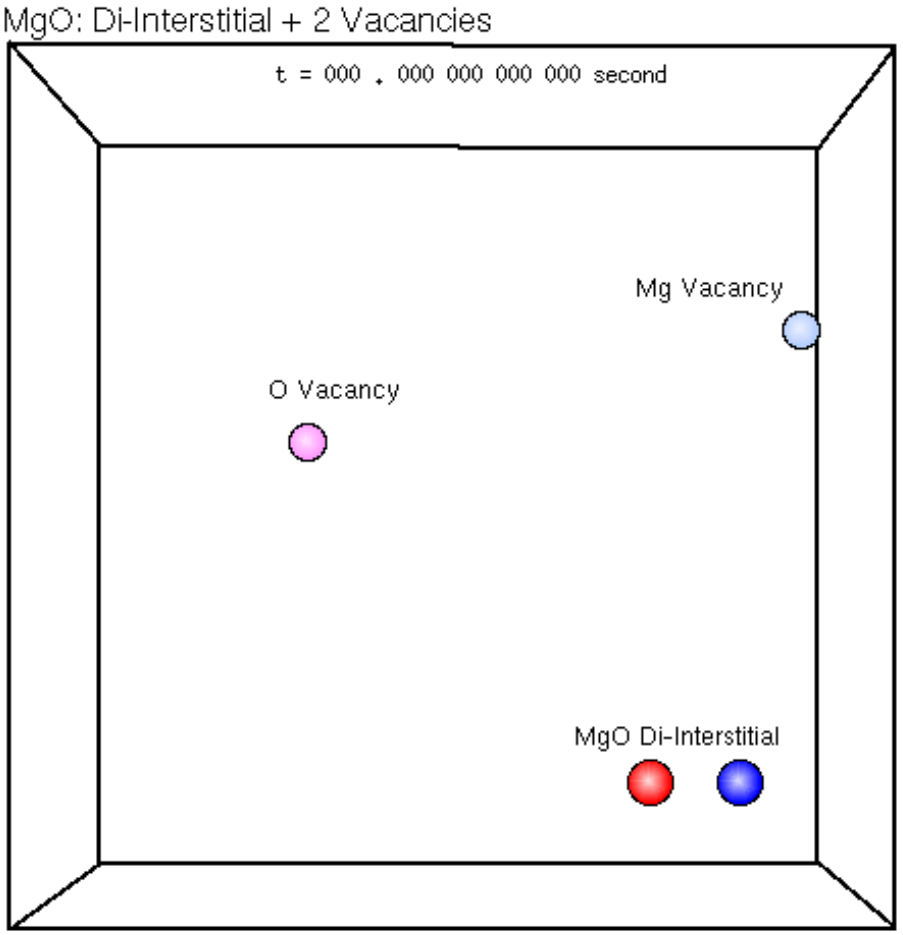
# Collision cascade

- Small energy collision cascade
- Primary knock-on atom (PKA) energy is 400 eV
- At the end of the cascade, 2 vacancies (light colors) and 2 interstitials (dark colors) remain



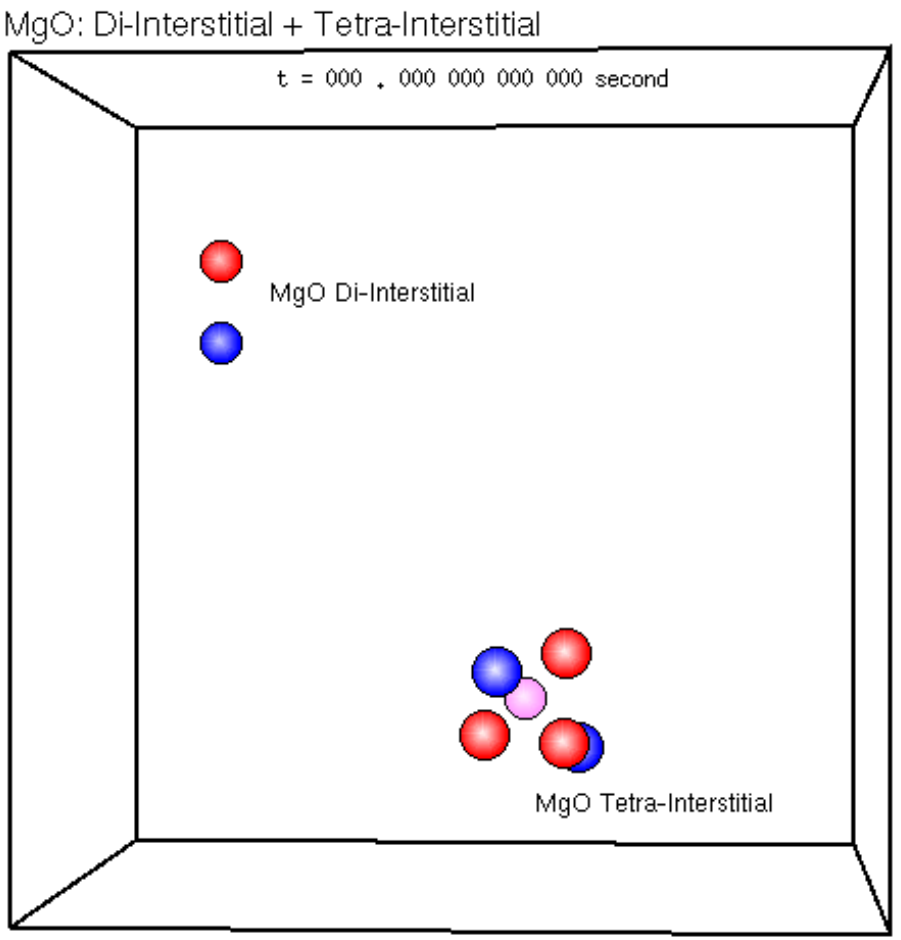
# TAD Simulation: Long-range Annihilation

- Begin with $I_2$ and two vacancies
  - Similar to end-state of cascade simulation
- $I_2$ attracted to charged vacancies, annihilating by 81 ms
- Annihilation via long range, concerted events involving many atoms
- Red=oxygen, Blue=magnesium
- Dark=interstitial, Light=vacancy



# TAD Simulation: Defect Aggregation

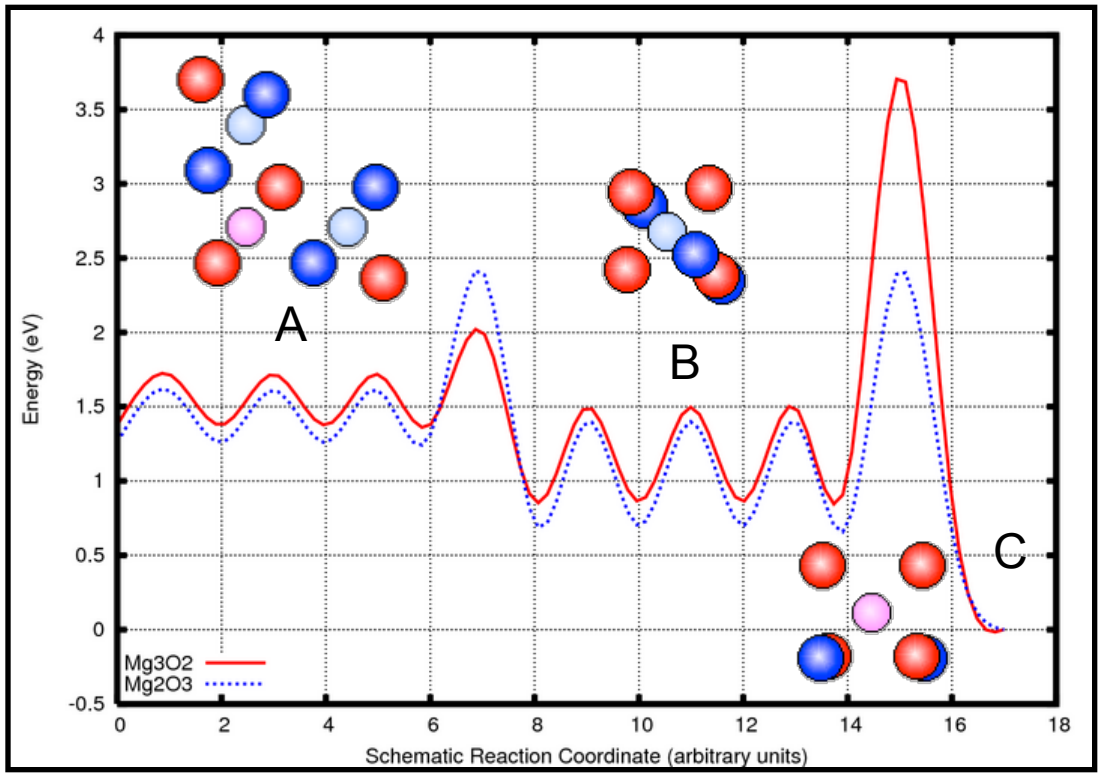
- Begin with $I_2$ and $I_4$
  - Defects found at end of collision cascade
- $I_2$ attracted to $I_4$, binds forming $I_6$
- Metastable $I_6$ diffuses very quickly
  - ns timescale at 300 K
  - diffusion is 1D along <110>
  - decay to ground state takes years
- Red=oxygen, Blue=magnesium
- Dark=interstitial, Light=vacancy




TAD simulation, Uberuaga et al, 2003

# Cluster dynamics: Kinetics of the pentamer cluster in MgO

- Two versions of pentamer:
  - $Mg_2O_3$
  - $Mg_3O_2$
- Both can exist in 3 forms
- Each has unique diffusive characteristics
  - A: diffuses quickly in <110> direction
  - B: diffuses more slowly, again in <110> direction
  - C: immobile at 300K
- A, B and C behave similarly for both pentamers
- But decay between forms is different

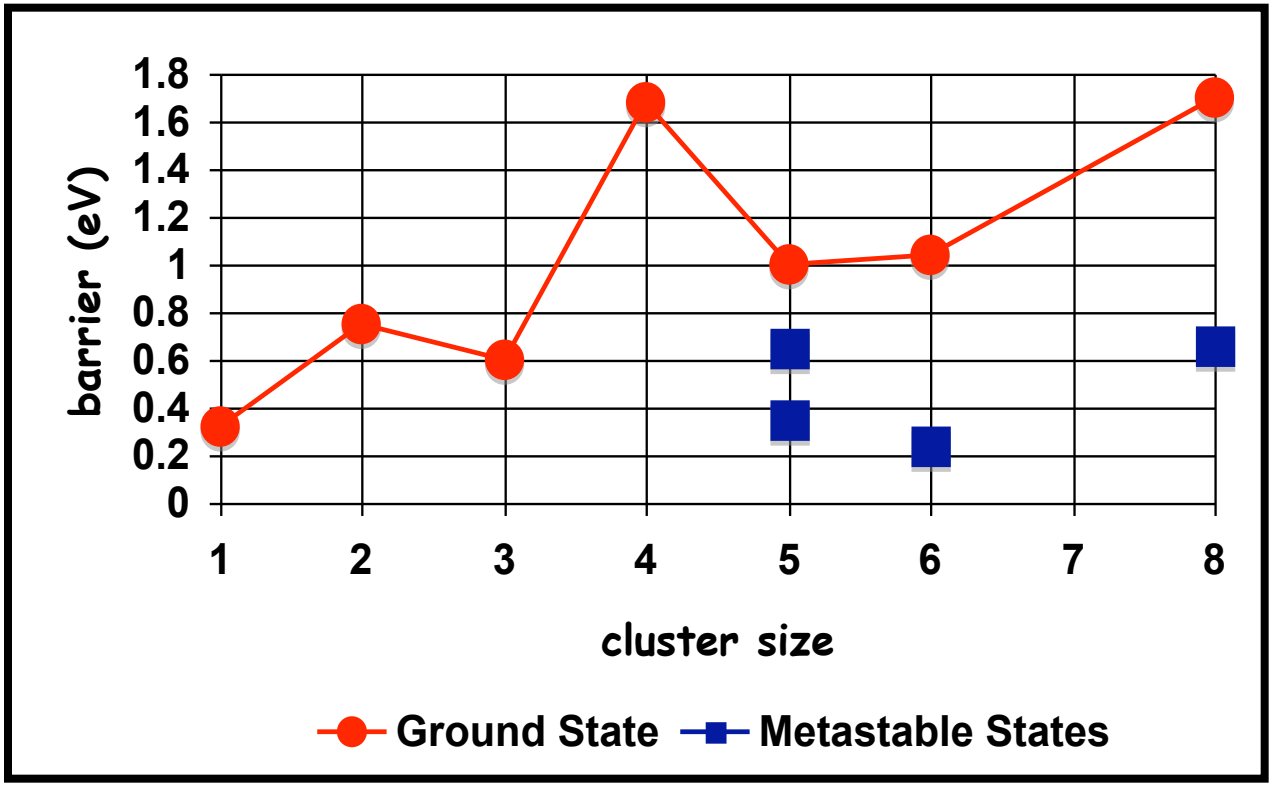



- Encounters of MgO+$MgO_2$ can form any type of $Mg_2O_3$
  - 10 simulations: 1 forms A, 7 form B, 2 form C

Uberuaga, et. al., *PRL* **92**, 115505 (2004); *PRB* **72**, (2005); *NIMB* **28**, 260 (2005)

# Interstitial cluster kinetics in MgO

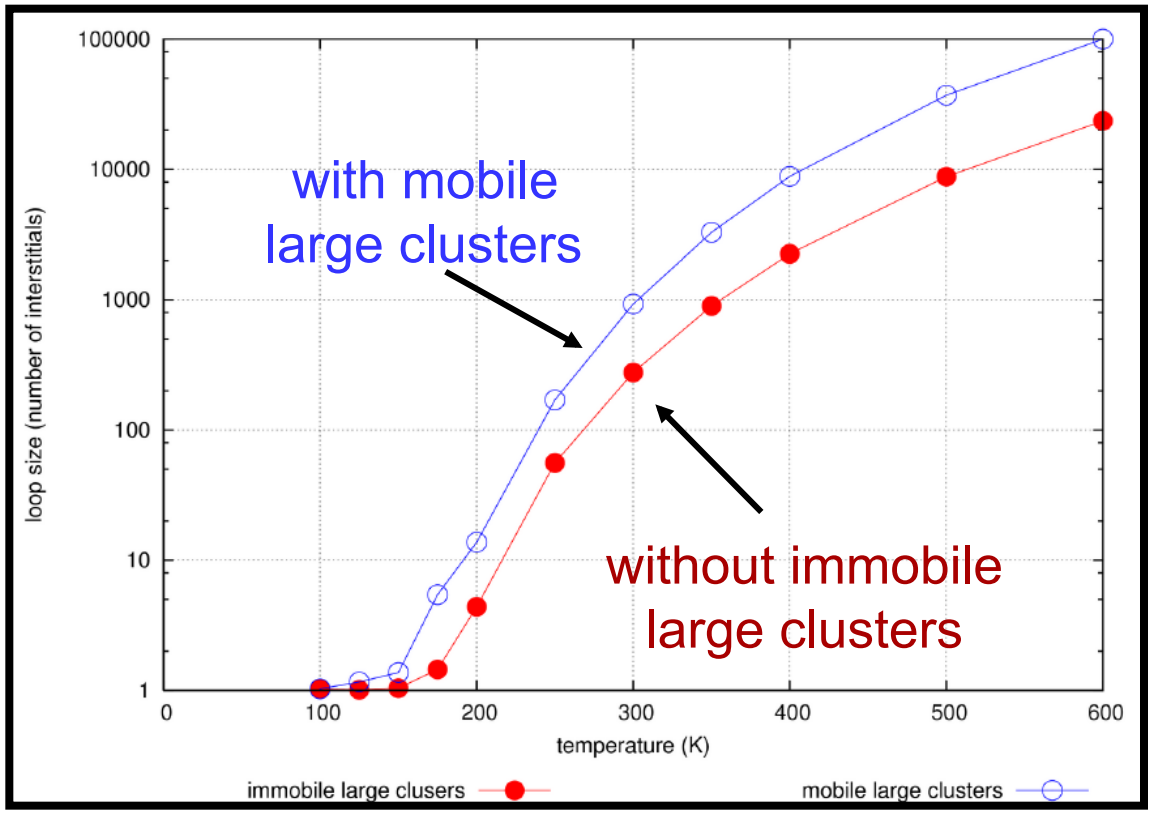
- Diffusion barrier of ground state structures follow no clear pattern
- For clusters of size 5 and greater, there are metastable structures that diffuse faster than the ground state




Uberuaga, et. al., *PRL* **92**, 115505 (2004); *PRB* **72**, (2005); *NIMB* **28**, 260 (2005)

# Effects of cluster mobility on observables

- 1-D reaction rate theory
  - Mobilities from TAD
  - Steady-state conditions
- Size of loops increases by more than 3 times when large clusters are mobile
  - "large" clusters contain more than 1 interstitial
- Enhanced defect mobility results in fewer, larger loops




Uberuaga, et. al., *PRL* **92**, 115505 (2004); *PRB* **72**, (2005); *NIMB* **28**, 260 (2005)

# Why long time simulations were needed?

- TAD simulations revealed that aggregation of interstitials leads to metastable interstitial cluster structures with high mobilities
- Critical that evolution observed at low temperature as lifetime of metastable clusters at high temperature would be short and possibly missed if simply performed high-temperature MD
  - Decay barriers 0.5 – 2 eV
  - Migration barriers 0.3 – 2 eV

A Parallel-Replica Study

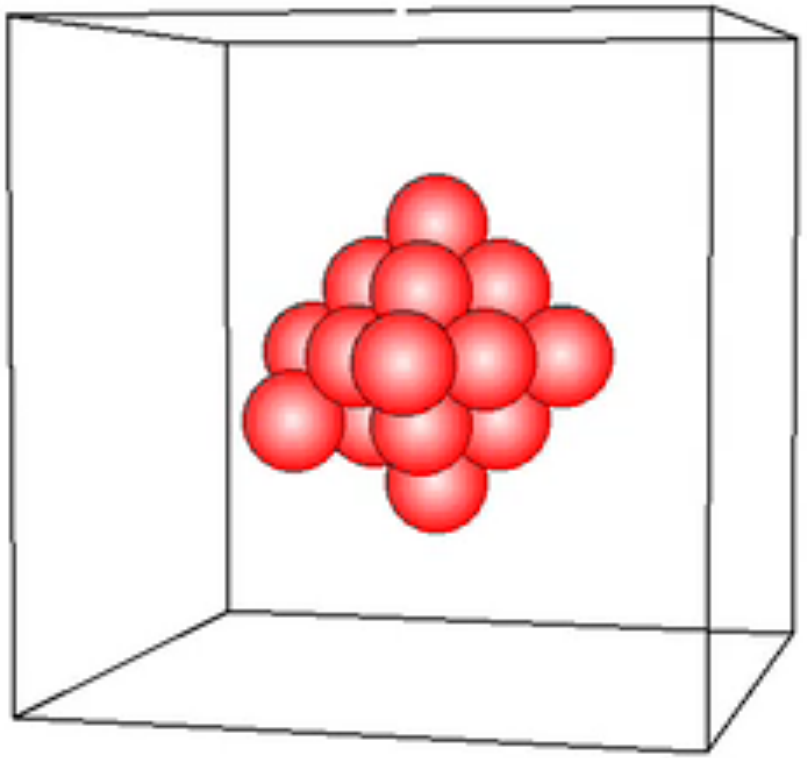
# VACANCY VOID ANNEALING IN CU

# Vacancy void annealing in Cu

- Goal:
  - Understand vacancy aggregation/void formation
  - Probe kinetics of vacancy voids
- Method:
  - Parallel-replica dynamics: explore long-time behavior of voids
  - Molecular dynamics: obtain statistics on possible pathways
  - Nudged elastic band (molecular statics): characterize pathways
- Reference:
  - Uberuaga, Voter, Hoagland, and Valone, PRL **99**, 135501 (2007).

# Long time annealing of 20 vacancy void in Cu

- EAM Cu
- Parallel-replica simulation of 20-vacancy void annealing at 400 K
  - 20 vacancies is one too many for "perfect" void
- Total simulation is 7.82 μs
- At 1.69 μs, void transforms to SFT
- Run on 39 processors for 15 days
- Efficiency = 79%
- *Equivalent single processor time: 1.3 years*



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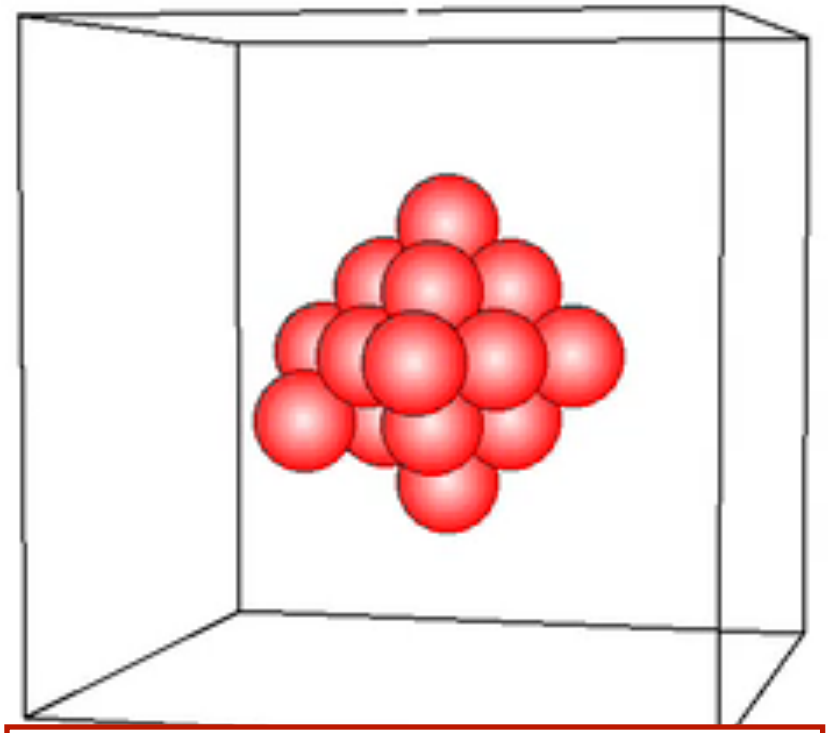
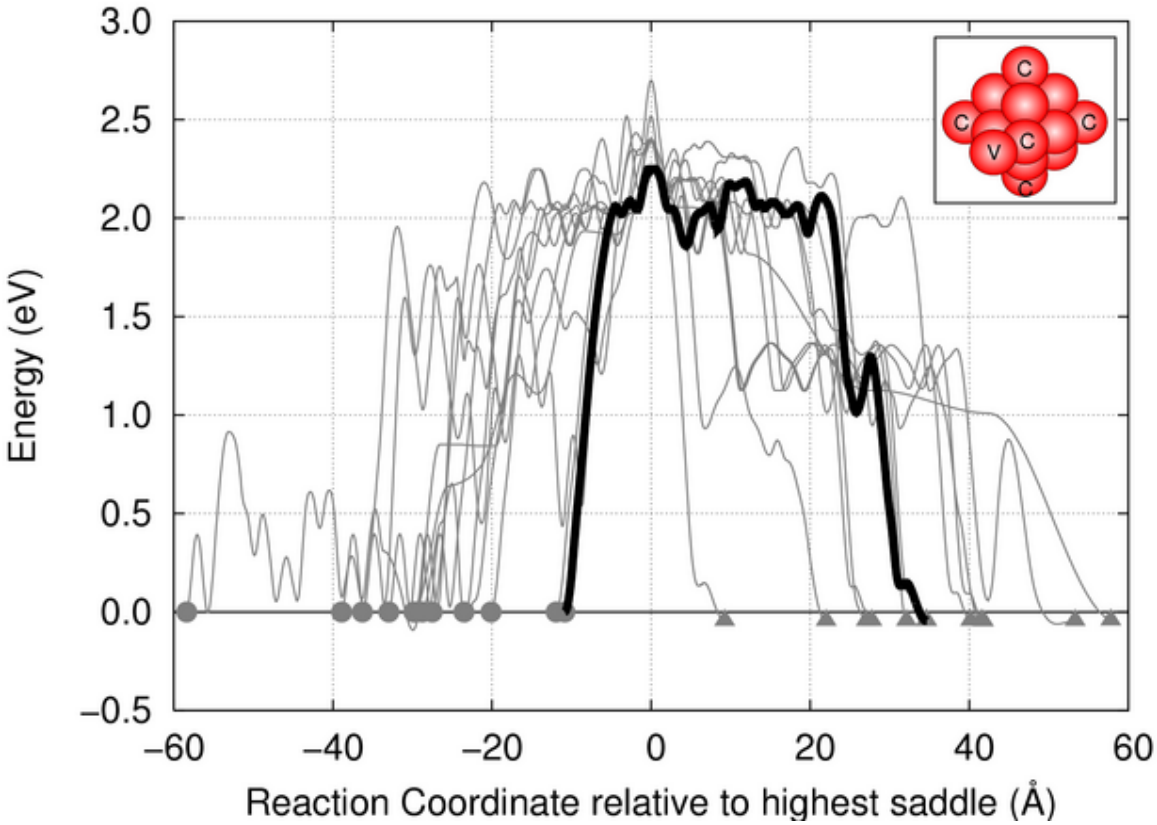


New transformation pathway for the formation of stacking fault tetrahedra (SFTs)

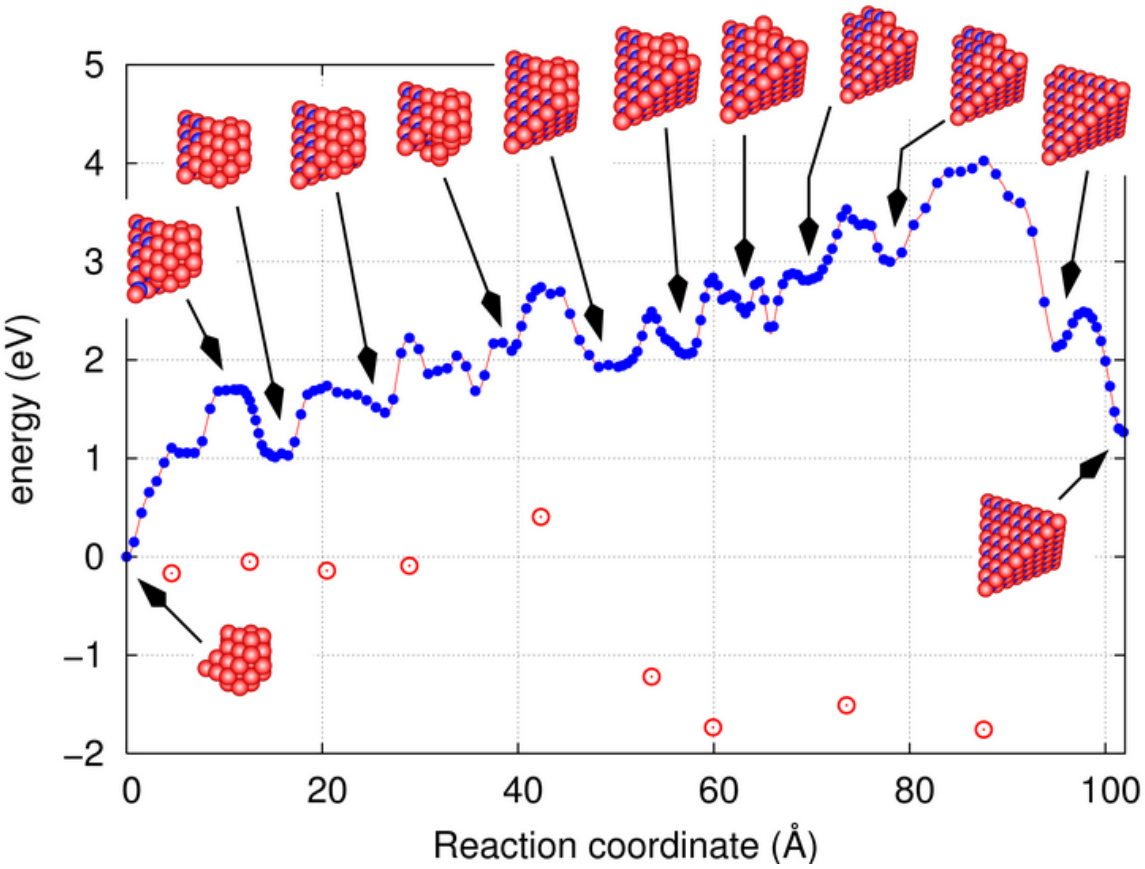
# Transformation pathway for 20 vacancy void

- Full path for transformation to SFT calculated with NEB
- Initial barrier is > 2 eV
  - Should have taken >$10^5$ years at 400K to occur (assuming standard prefactor)
- Vineyard prefactor for first step between $10^{36}$ and $10^{43}$ Hz



# Void to SFT transformation: 45 vacancy void in Cu

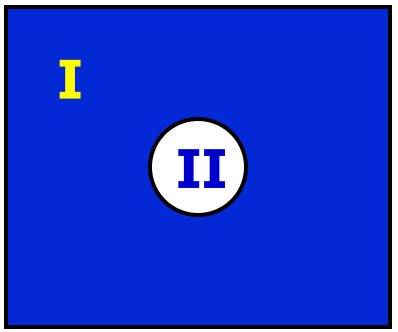
- Par-rep of 45 vacancy void at 475 K
  - 39 processors
  - 39% efficiency
  - 5.6 days
    - Effective 1 CPU time: 85 days
  - 0.24 μs
- Figure is minimum energy path at constant volume
- Overcomes a very large internal energy barrier (~4 eV) at 475 K
- Free energy barrier is much lower, as estimated by open symbols



# Prefactor for Transformation

- Barrier for 20-vacancy void is between 2.3 and 2.7 eV
  - Assuming a standard prefactor (~$10^{13}$ Hz), would take $10^6$ years to occur at T=400 K
  - Observed waiting times are 1-15 ns
  - Prefactor observed from dynamics: $10^{38}$ Hz; calculated with Vineyard: $10^{43}$ Hz
  - *Prefactor is anything but standard!*

- Origin of Prefactor
  - View material containing void as partitioned into two regions
    - Region I: Cu
    - Region II: void
  - Before transition, volume of Cu is Region I volume
  - After, volume of Cu is Region I + Region II
  - Entropy change $\Delta S$ due to volume change $\Delta V$: $\Delta S=\alpha B \Delta V$
    - $\alpha$=coefficient of thermal expansion, B=bulk modulus
  - Assuming $\Delta V$=10 atomic volumes ⇨ $\Delta S=67.5/k_B$ ⇨ prefactor enhanced by factor of $10^{29}$
  - Consistent with observed/calculated prefactor



# Why long time simulations were needed?

- Once system is in corner state, time scale for void → SFT transformation very quick, ns
- However, time to reach corner state can be very long, 1.7 μs at 400 K
- Parallel-replica was critical for reaching time scales for surface vacancy to sample surface configurations and discover corner state

A Temperature Accelerated Dynamics Study

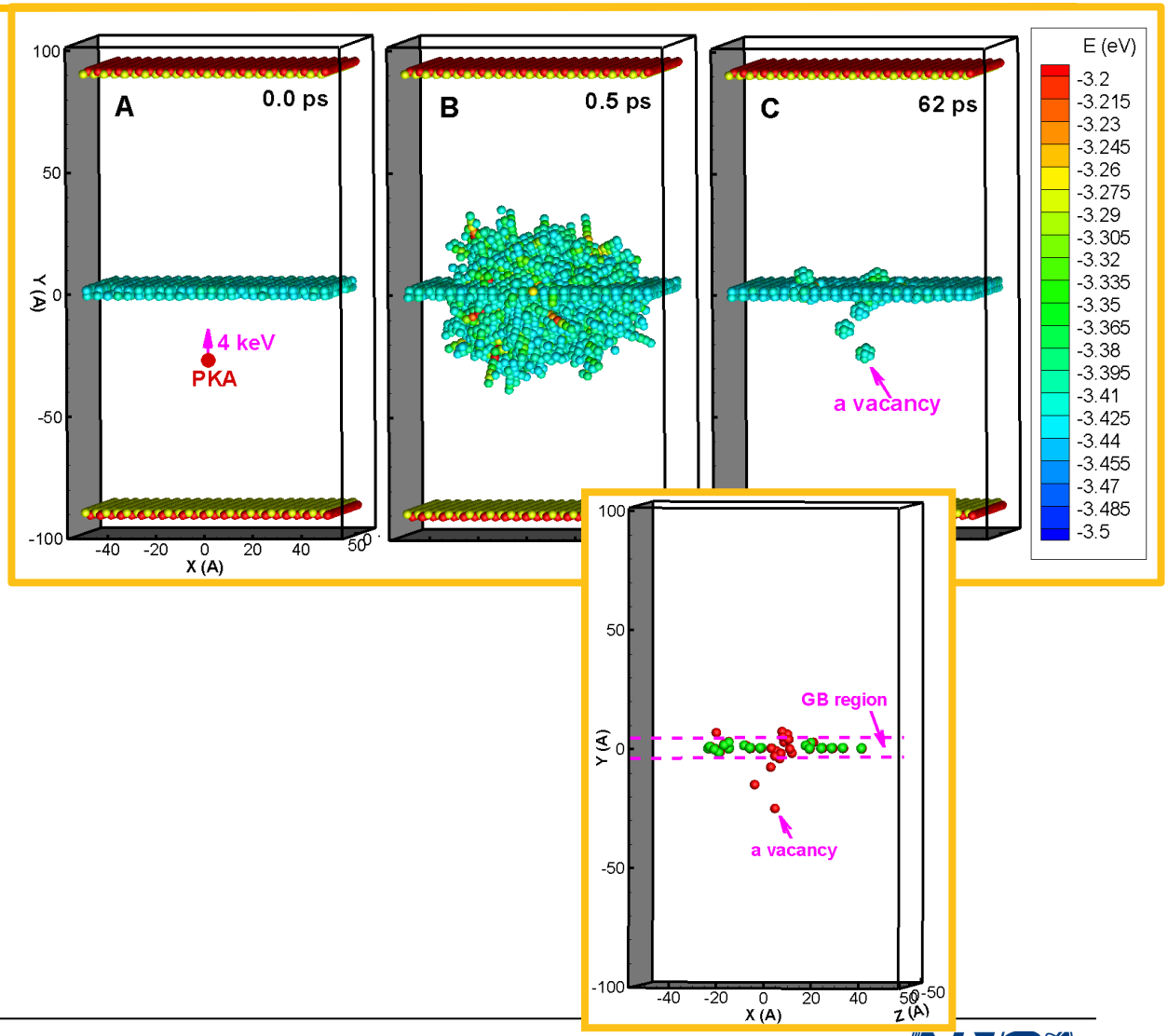
# DAMAGE PRODUCTION AND EVOLUTION NEAR GRAIN BOUNDARIES

# Defect-Boundary Interactions in Cu

- Goal:
  - Understand how grain boundaries modify radiation damage production and evolution
  - Identify regimes where different processes may be important
- Method:
  - Molecular dynamics: defect production in cascades
  - Molecular statics: defect thermodynamics near boundaries
  - Temperature accelerated dynamics: annealing of defects near boundaries
- Reference:
  - Bai, Voter, Hoagland, Nastasi, and Uberuaga, Science **327**, 1631 (2010).

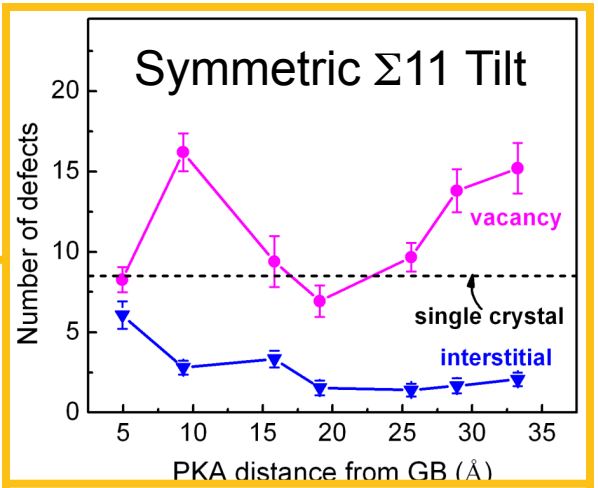
# Cascades near a Σ11 symmetric tilt grain boundary

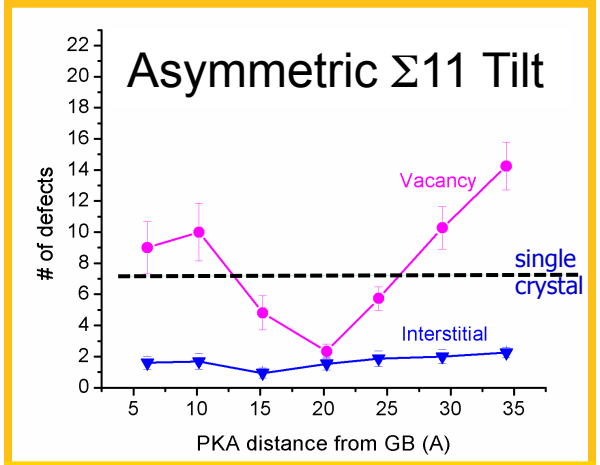
- Snapshots of a 4 keV cascade initiated 25 Å below Σ11 symmetric tilt GB at 300 K
- Atoms colored by energy
- After cascade, interstitials absorbed by boundary, excess vacancies produced in bulk

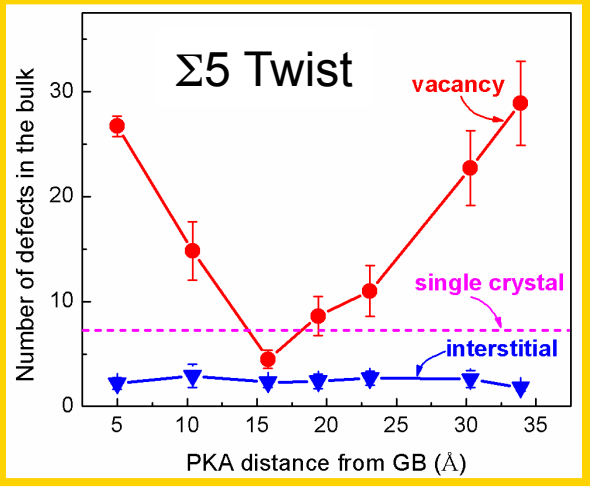


# Damage production near GBs

- Number of surviving defects in bulk as a function of PKA distance *d* from GB
- Each GB preferentially absorbs interstitials over vacancies
- Often, so many interstitials absorbed that excess vacancies created in bulk
- Details depend on GB structure

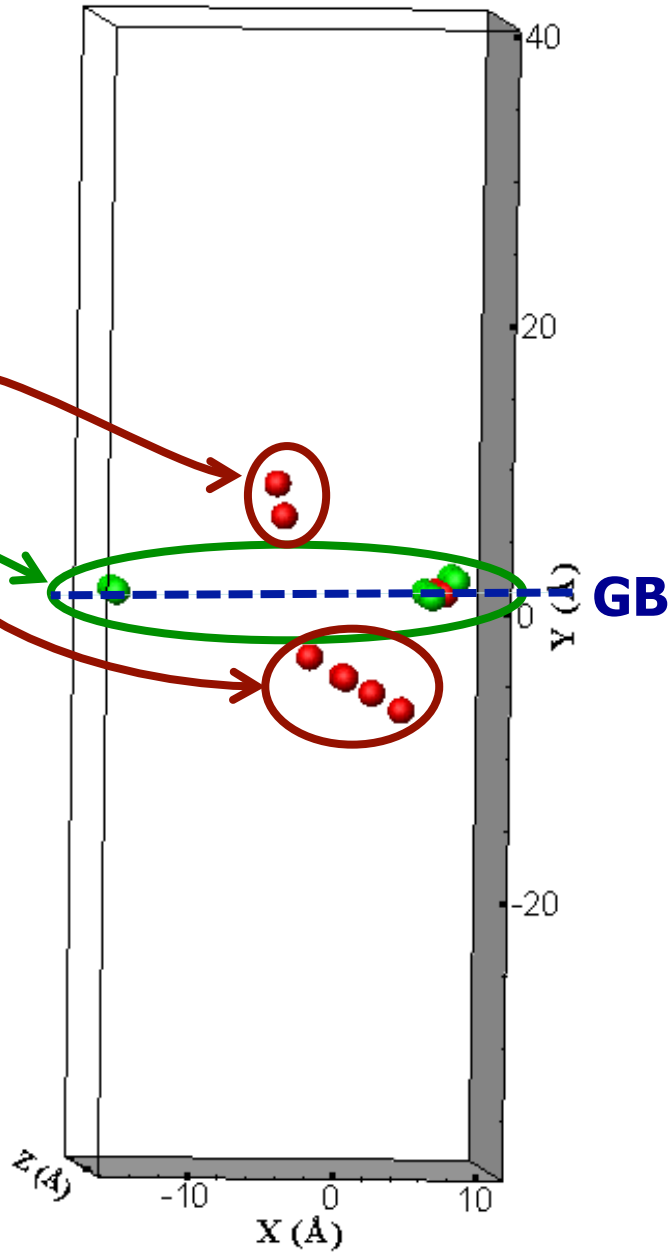


# Evolution of residual damage

- After cascade, GB is loaded with interstitials, vacancies reside in bulk
- Temperature accelerated dynamics (TAD) simulations to explore long-time evolution
- With relatively small barriers (0.1-0.2 eV) compared to bulk vacancy barrier (0.69 eV), interstitials can 'emit' from boundary and annihilate vacancies



# Snapshots of TAD simulation

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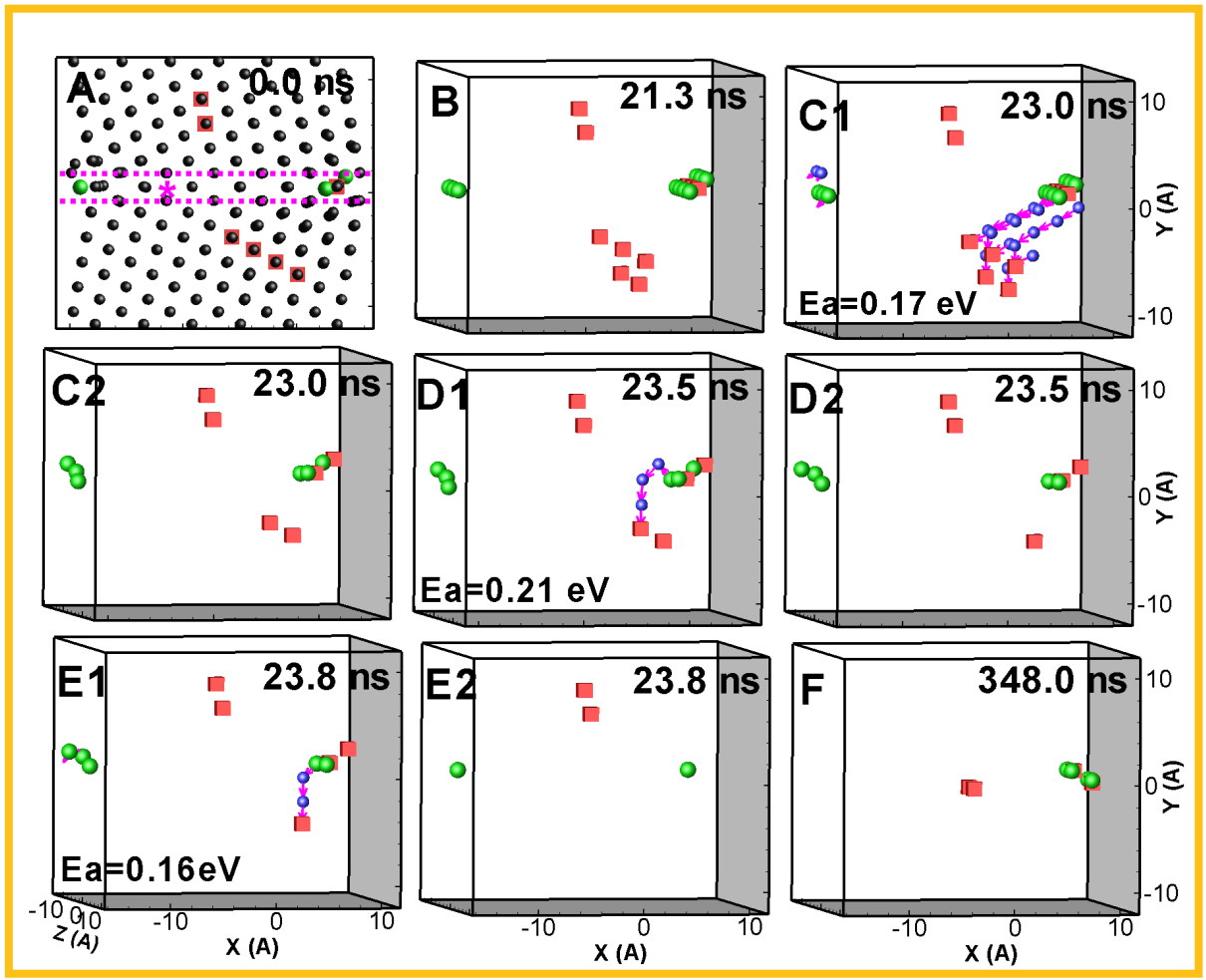
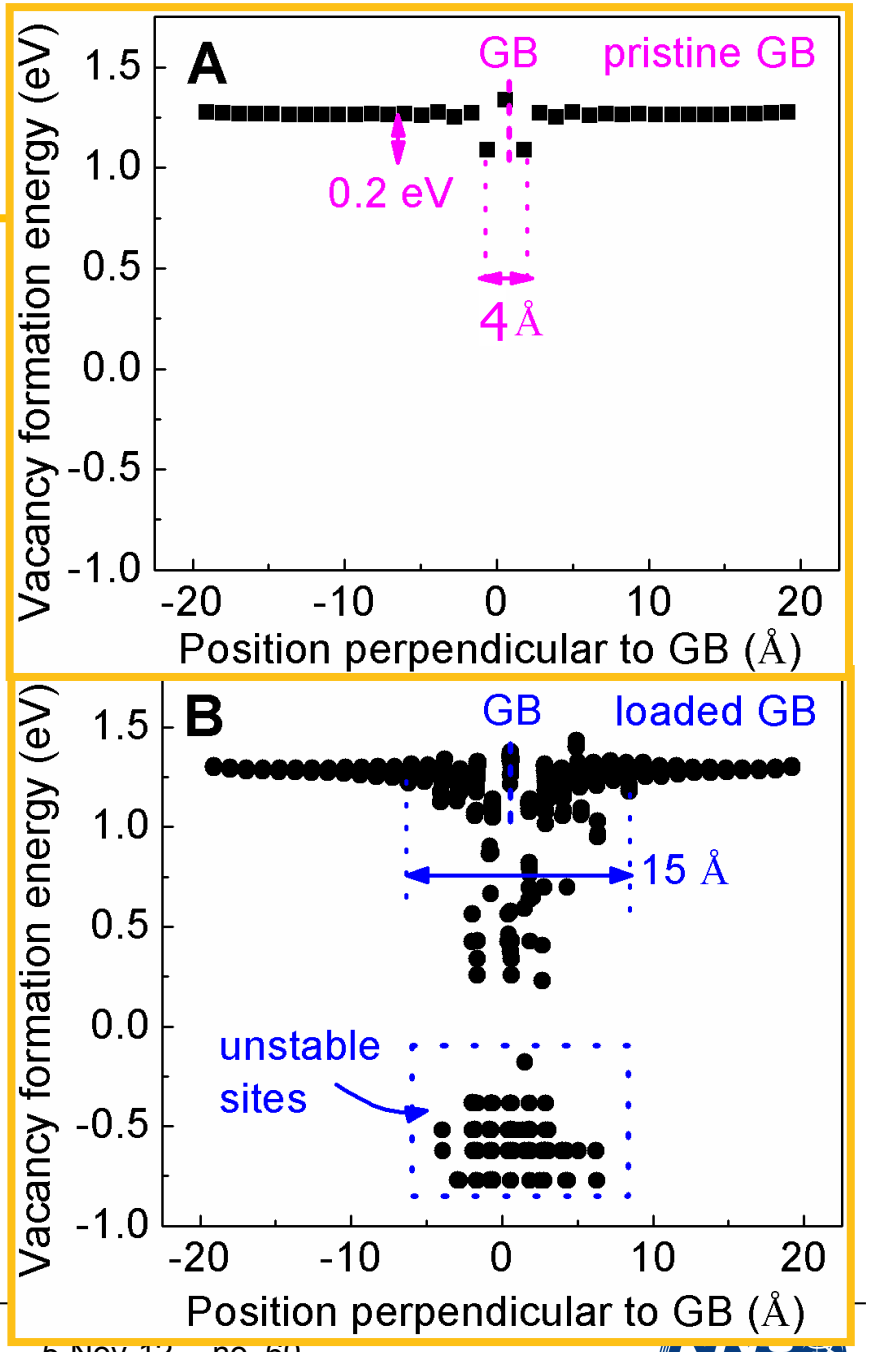
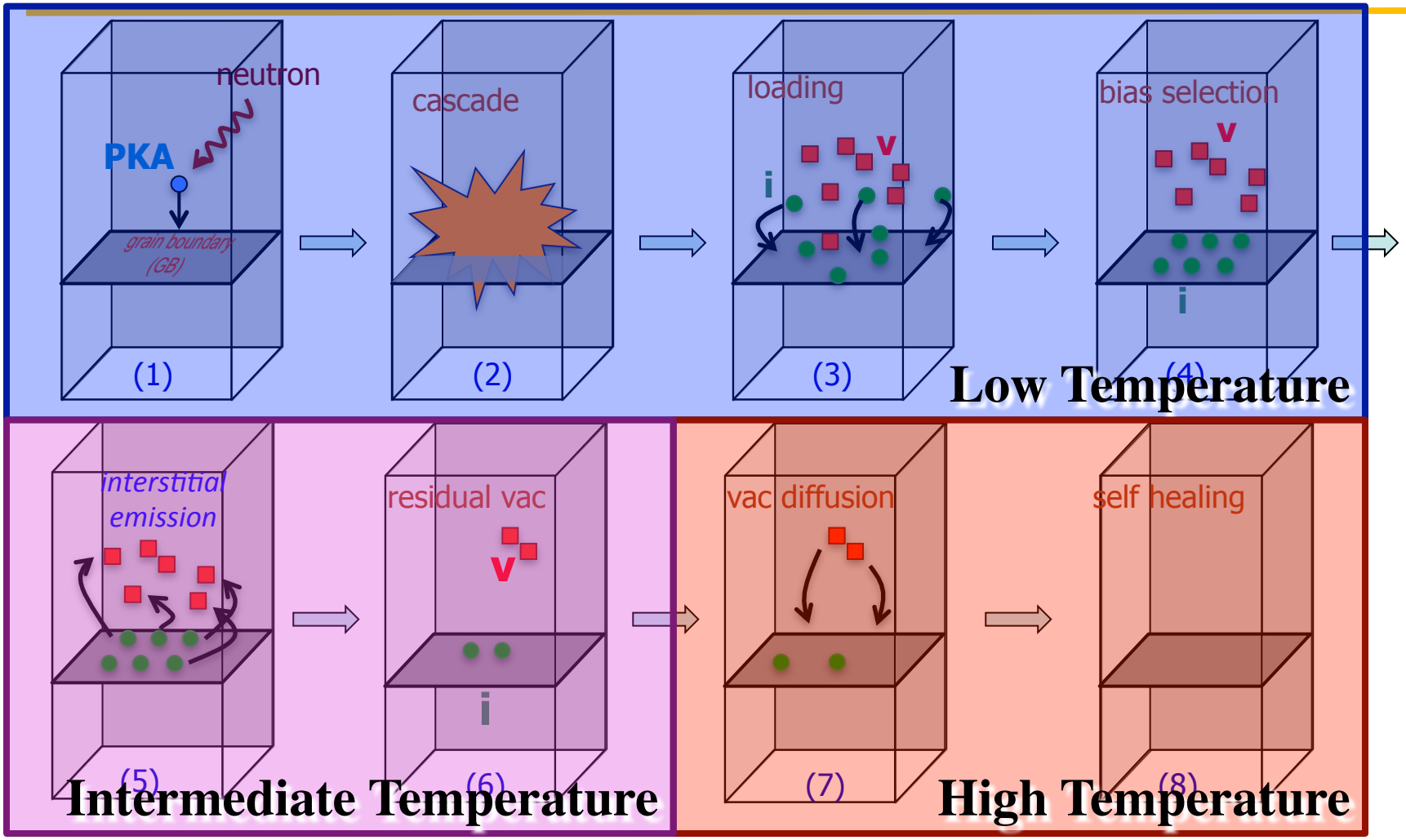


# Interaction of loaded boundary with vacancies

- Vacancy-boundary interaction sensitive to interstitial loading at GB
  - Artificially create interstitial-loaded GB to study behavior
- Before loading, GB and vacancy interaction is very weak
- Upon loading, range and strength of GB interaction with vacancies much stronger and longer-ranged
- Interstitial emission can occur for vacancies as far as 1 nm from boundary
- Similar effects seen for other boundaries



# Radiation damage regimes in nanomaterials



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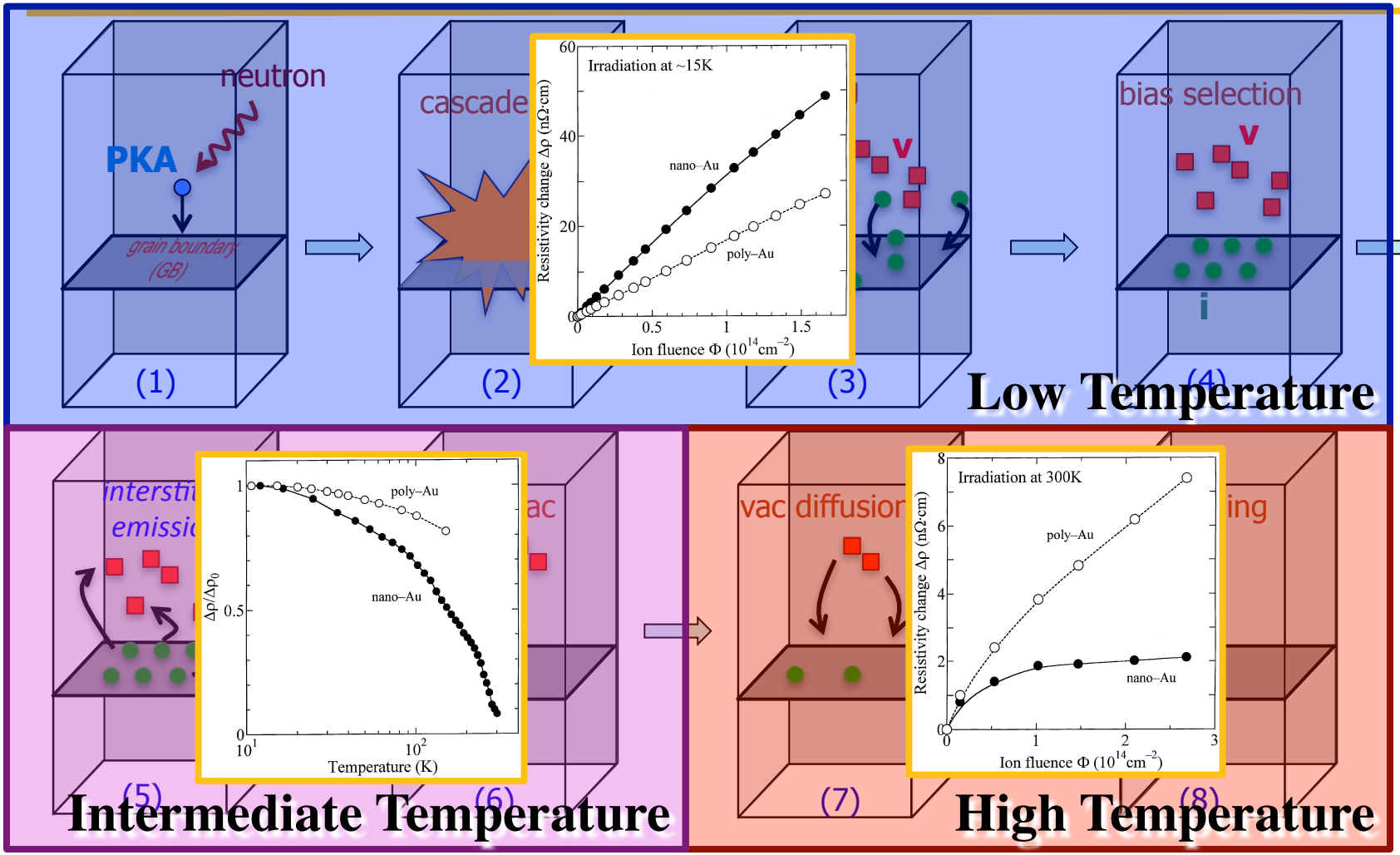



*Expts: Chimi et al. JNM 297, 355 (2001).*

# Why long time simulations were needed?

- Typical assumption is that boundaries are infinite sink for defects
- TAD revealed that defect-boundary interactions are enhanced at damaged boundaries
- Result possibly could have been found via MD, however only because time scales shortened by new mechanism

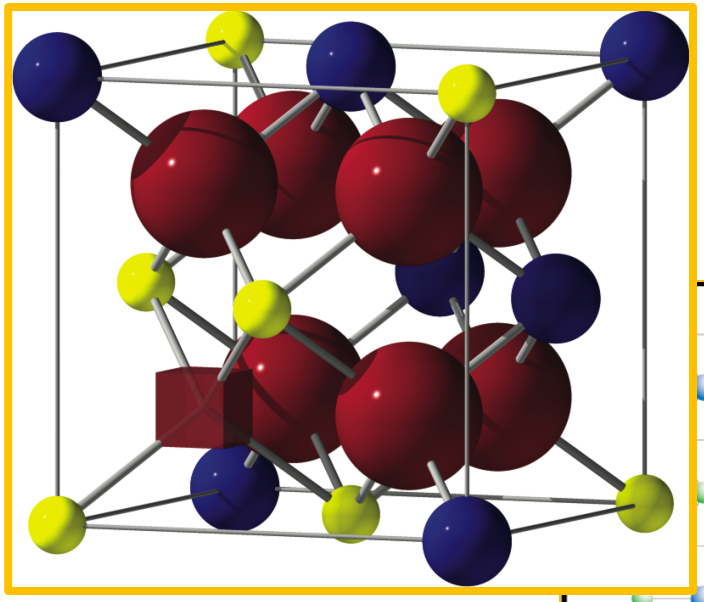
A Temperature Accelerated Dynamics Study

# DEFECT PRODUCTION AND RECOVERY IN PYROCHLORE

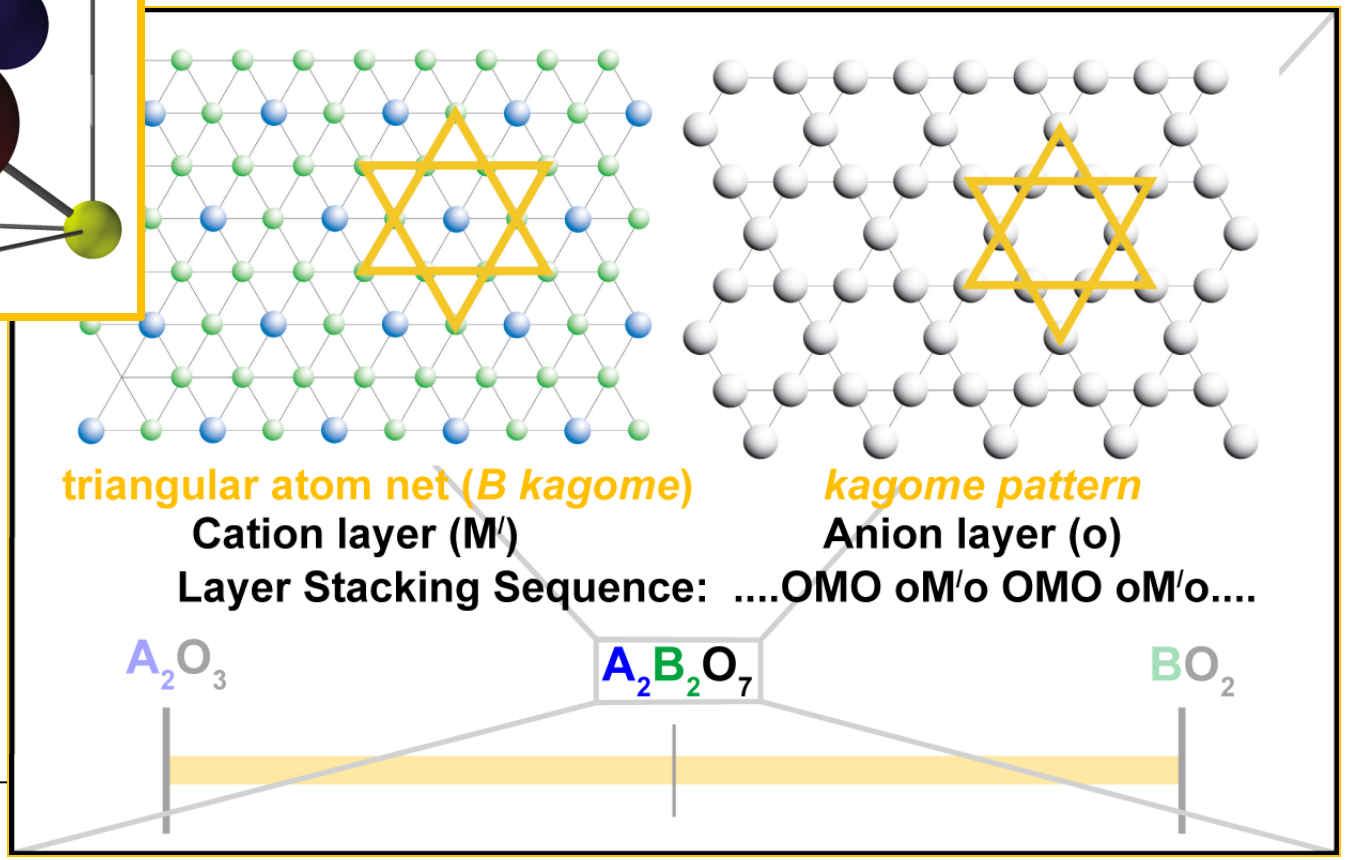
# Defect Production and Recovery in Pyrochlore

- Goal:
  - Examine the early stages of damage production and evolution in pyrochlore
  - Understand the connections between damage mechanisms and disorder
- Method:
  - Experiment: unit mechanism of swelling versus dose
  - Density Functional Theory: volumes of formation of point defects
  - Temperature accelerated dynamics: long time annealing of Frenkel pairs
- Reference:
  - Li et al, Phys. Rev. Lett. **108**, 195504 (2012).

# Structure of Pyrochlore



- Pyrochlore is an oxygen-deficient fluorite derivative



# Definition of an Order-to-Disorder (*O-D*) Transformation in a Fluorite Structural Derivative

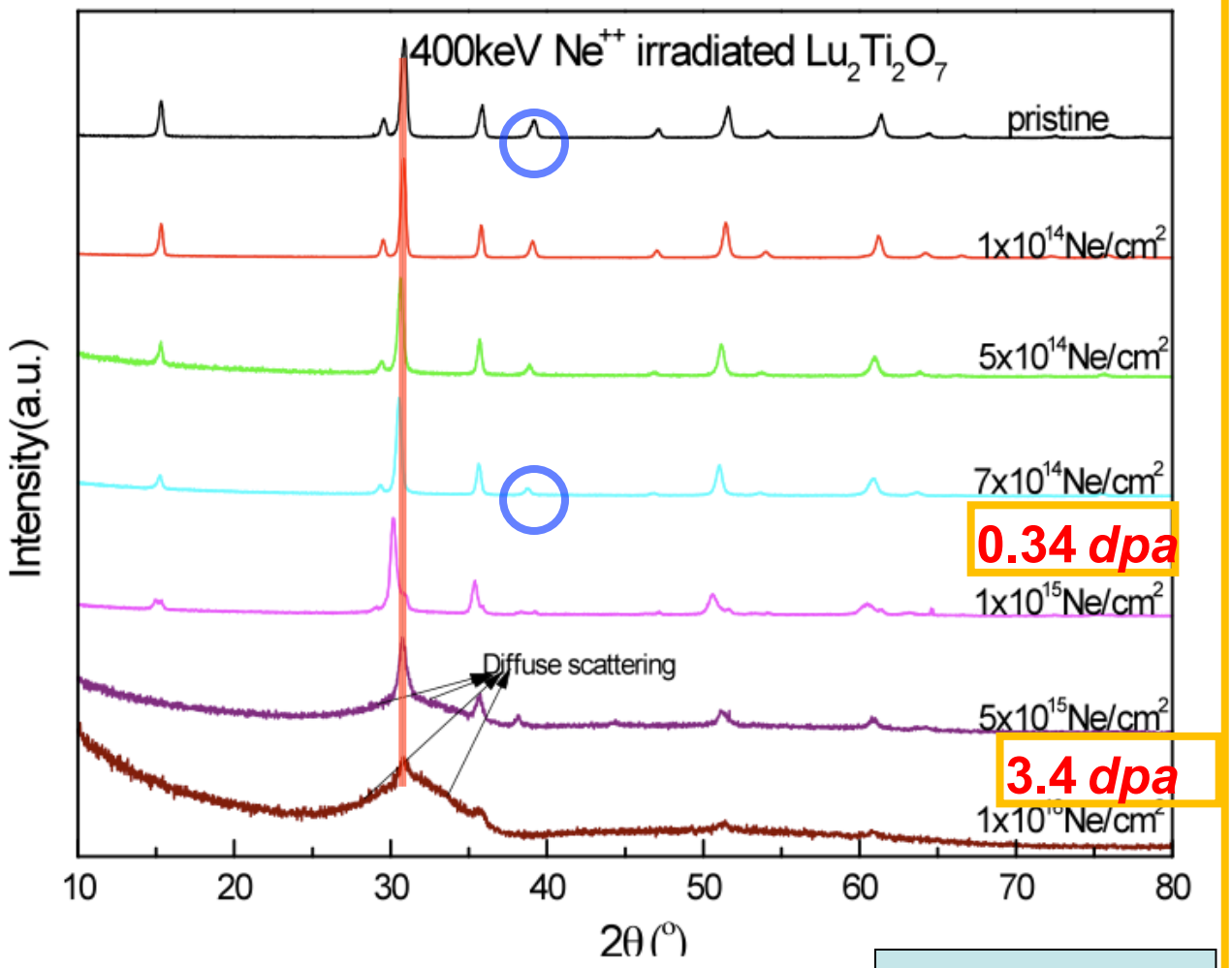
- Disordering propensity hypothesized to be a key indicator of radiation tolerance in complex oxides
  - *Science* **4**, 748 (2000), *Nature Materials* **6**, 217 (2007)

*O-D* defect reaction pair

$$\left\{ \begin{array}{ll} A_A + B_B \rightarrow A_B + B_A & \text{(cation antisite formation)} \\ O_O \rightarrow V_O + O_i & \text{(anion Frenkel formation)} \end{array} \right\}$$

# Grazing Incidence X-ray Diffraction (GIXRD)

- GIXRD as a function of fluence in $Lu_2Ti_2O_7$ irradiated with 400 keV $Ne^{++}$
- Two effects:
  - Peaks shift position
  - Some peaks disappear while others do not

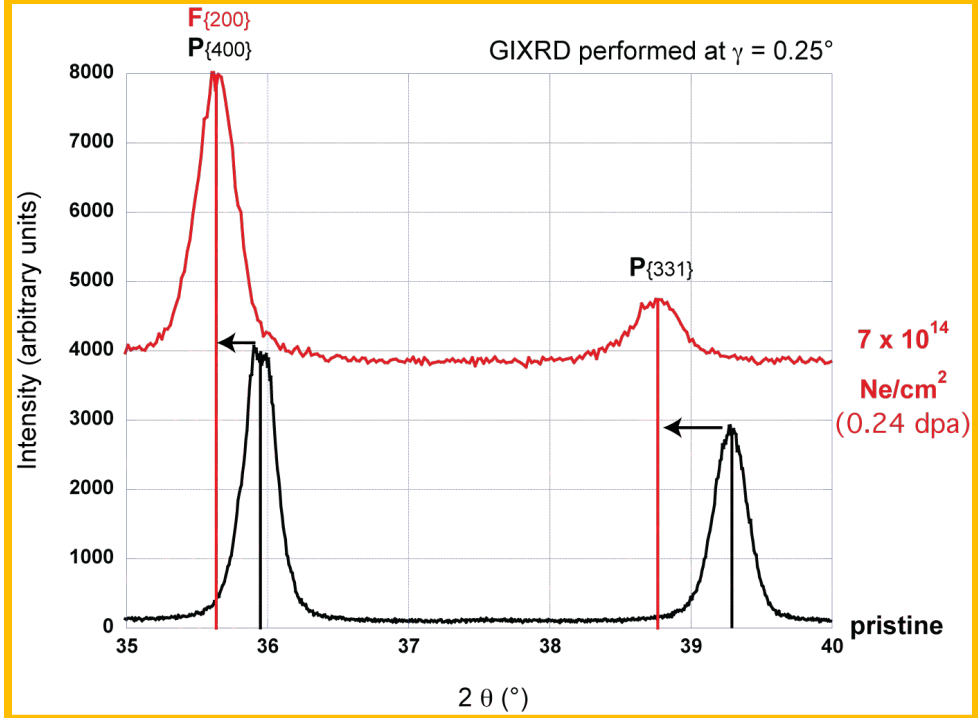



**GIXRD angle**
**γ = 0.25°**

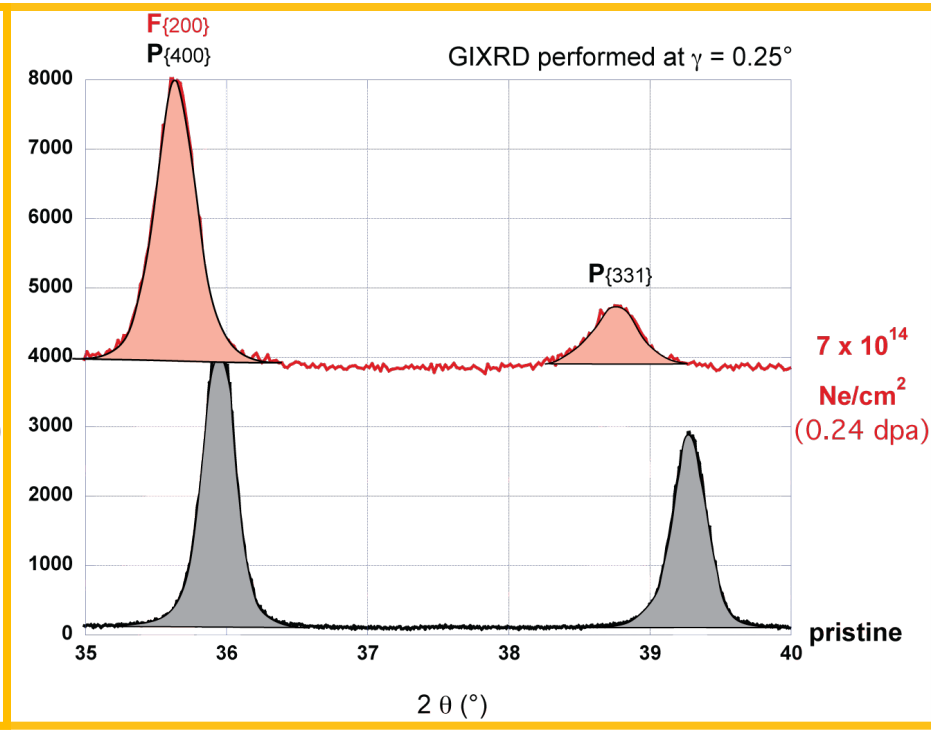
# GIXRD intensity versus scattering angle (2θ) and fluence

- Characterize both peak shift and changes in relative intensity vs fluence

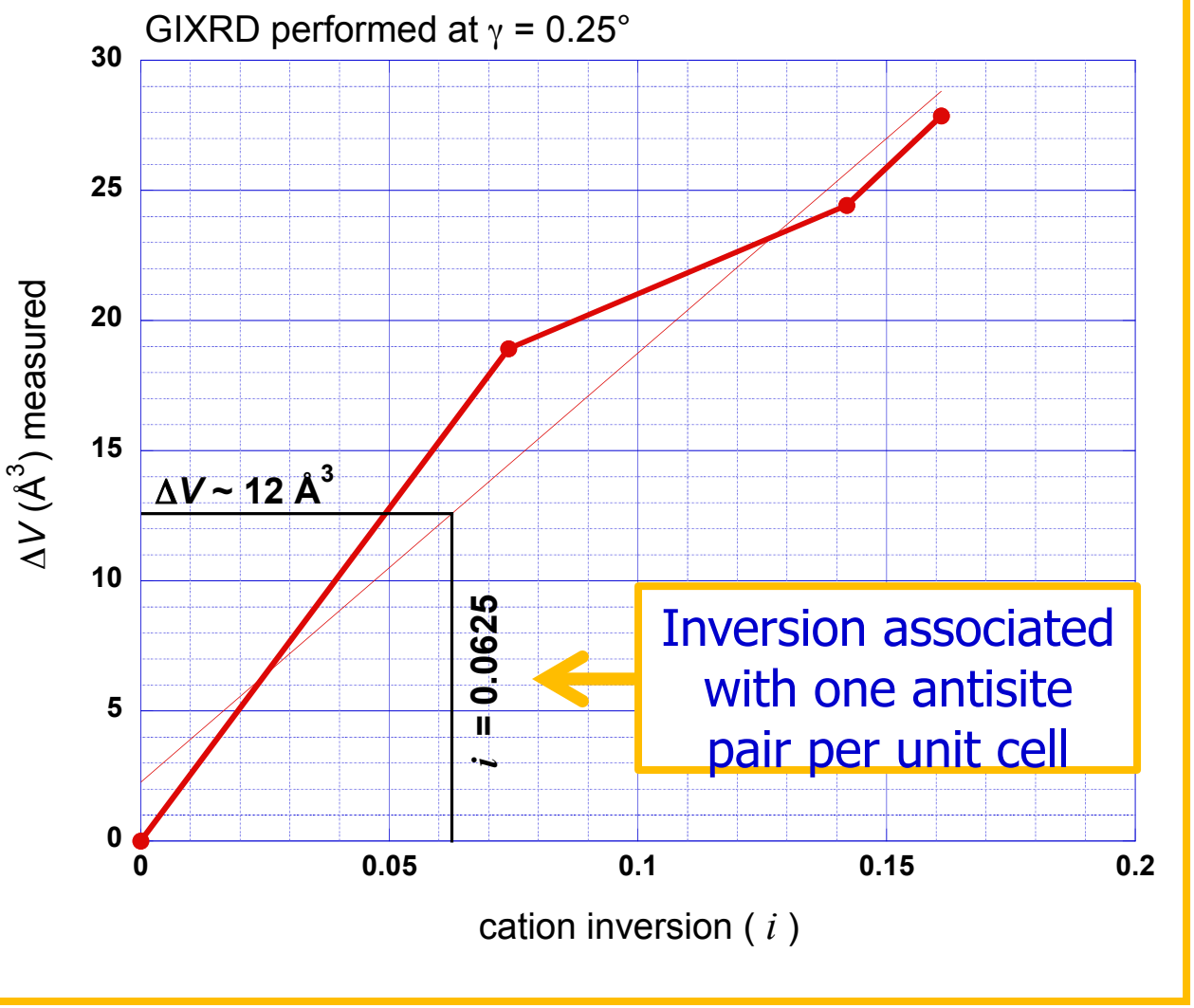
***Shifts related to dimensional changes***




***Changes in relative intensity are a measure of disorder***



# Change in unit cell volume versus cation inversion (*i*)

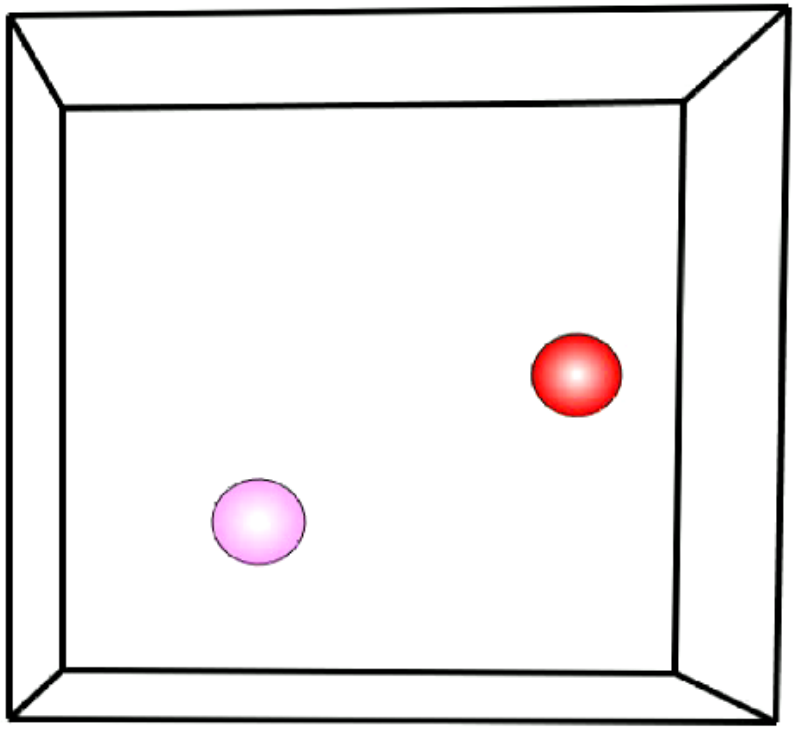


# Density Functional Theory: Defect Properties

- Lowest energy defects are antisite pairs
- Volumes of formation for antisites better match experimental swelling for one antisite pair per unit cell: 17-20 $Å^3$ vs 12 $Å^3$

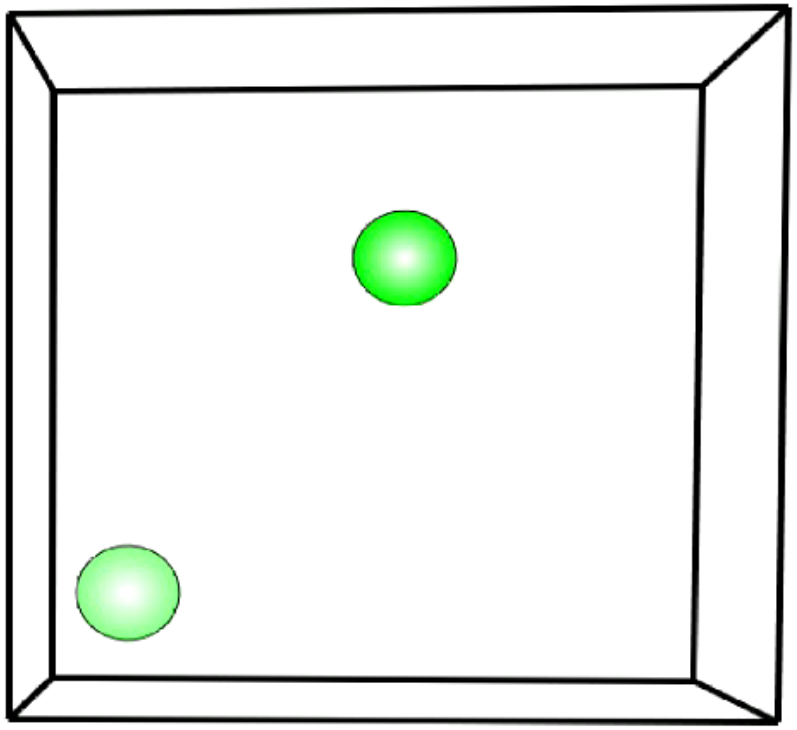
| *Defect* | *Formation Volume ($Å^3$)* | *Formation Energy (eV)* |
|---|---|---|
| Cation antisite pair (far apart) | 16.9 | 0.9 |
| Cation antisite pair (nearest neighbors) | 19.7 | 0.8 |
| Ti Frenkel pair | 53.5 | 3.3 |
| Lu Frenkel pair | 49.7 | 2.8 |

# TAD: Lu Frenkel Pair in $Lu_2Ti_2O_7$



- Lu Frenkel Pair: Lu interstitial and Lu vacancy
- Interstitial diffuses with barrier of about 1.0 eV until it gets close to vacancy, at which point antisite pair forms

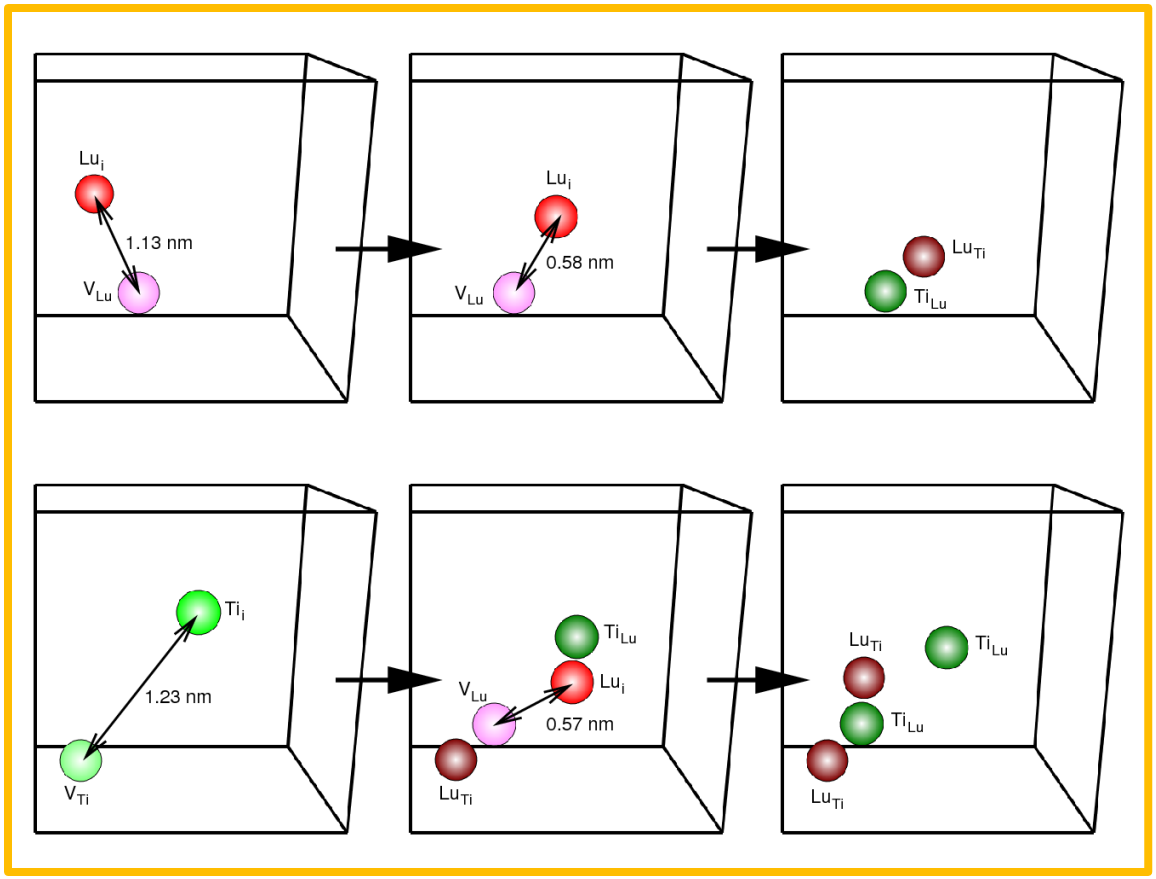
# TAD: Ti Frenkel Pair in $Lu_2Ti_2O_7$



- Ti Frenkel Pair: Ti interstitial and Ti vacancy
- Vacancy immediately decays to Lu antisite and Lu vacancy
- Ti interstitial also decays to Ti antisite and Lu interstitial
- When Lu interstitial reaches Lu vacancy, antisite pair formed

# Cation Frenkel pair evolution in $Lu_2Ti_2O_7$

- Temperature accelerated dynamics simulation of Frenkel pair recombination
- Both types of cation Frenkel pairs ultimately recombine to form antisites
  - In some cases, two antisite pairs can form
- Perfect annihilation is difficult (impossible)?
- However, barriers large (1-2 eV)
  - Not active at 77K, but fast at 1000K



# Putting it all together

- Experiment:
  - Inversion increases with irradiation fluence
  - Swelling associated with one antisite pair per unit cell: 12 $Å^3$
- Density functional theory:
  - Nearest neighbor antisites lowest energy defect
  - Formation volume of nearest neighbor antisites best match experiment
- Temperature accelerated dynamics:
  - Frenkel pair recombination leads to nearest neighbor antisites
  - Barriers for Frenkel pair recombination large
- **Conclusions**:
  - Perfect annihilation impossible
  - Antisites directly created in cascades

- ***Implication:***

***there is a high temperature reordering mechanism, as yet unidentified (vacancy mobility?)***

# Why long time simulations were needed?

- Identified mechanism for Frenkel pair recombination, showing it does not lead to recovery of perfect crystal
- Revealed that timescale for recombination is too long to occur under experimental conditions

# Summary

- AMD methods allow the study of processes not accessible to MD
- Often, results are very surprising
  - Many mechanisms that would be left out of e.g. KMC if intuition alone is used
  - New insights into kinetic processes, even in the simplest of materials

➔Probing long-time kinetics is crucial for understanding material evolution in complex environments